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THE Journal OF THE AMERICAN LEATHER CHEMISTS ASSOCIATION

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Vol. LVI FEBRUARY 1961 No. 2

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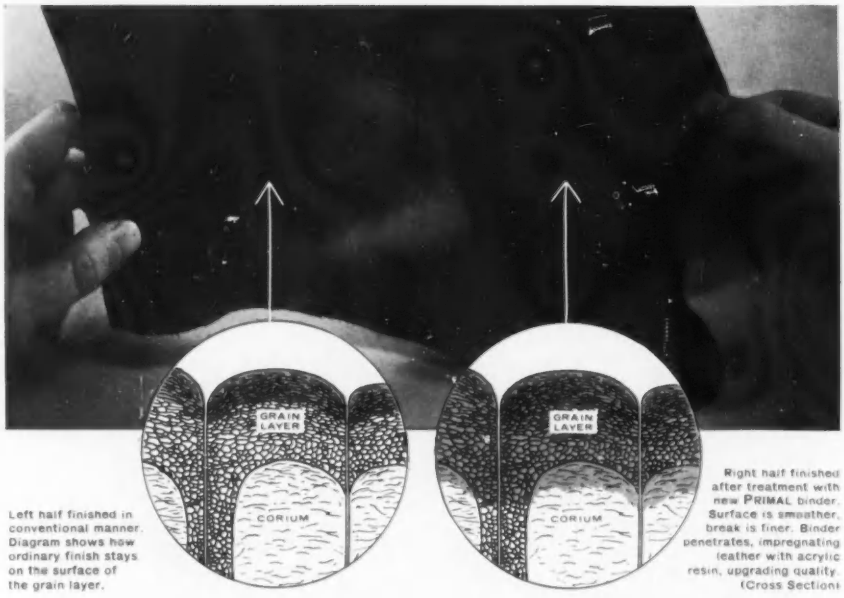

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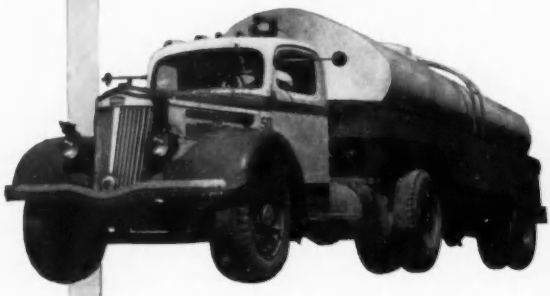

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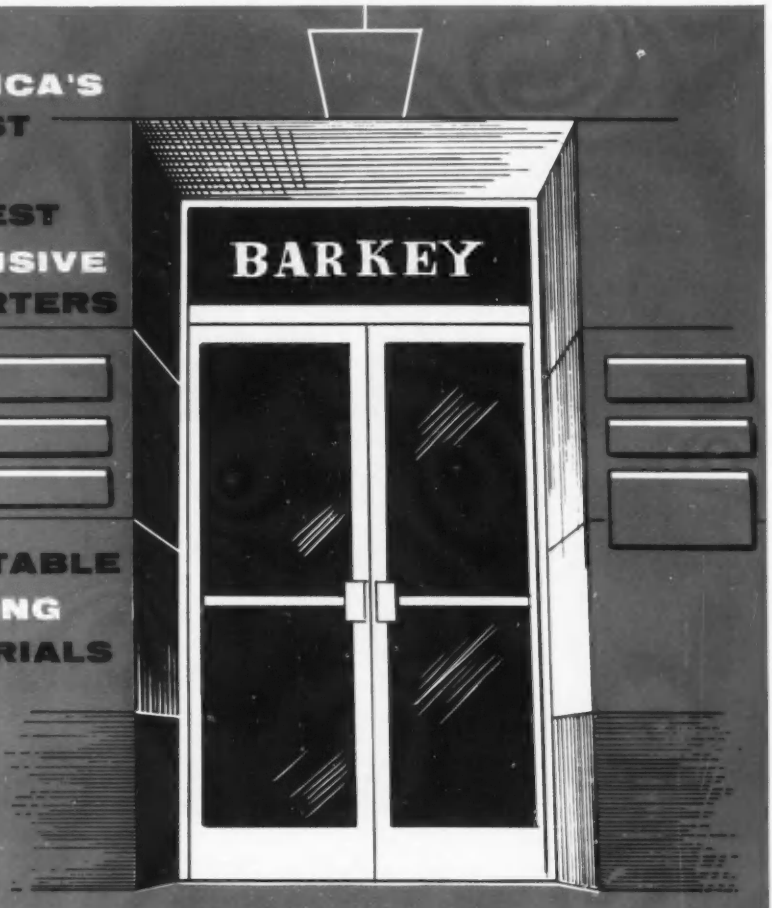

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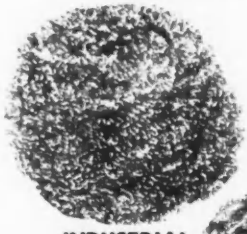

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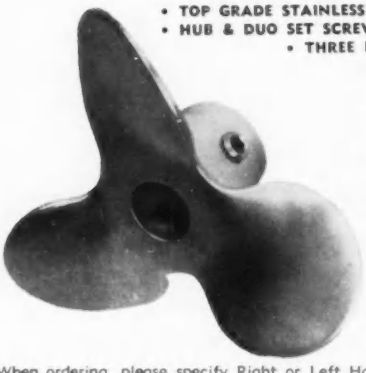

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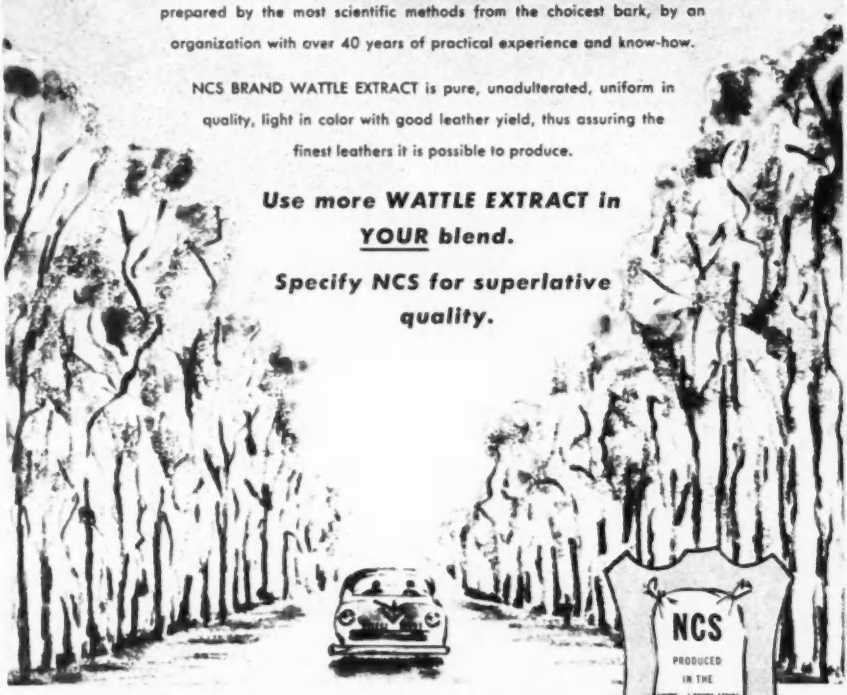

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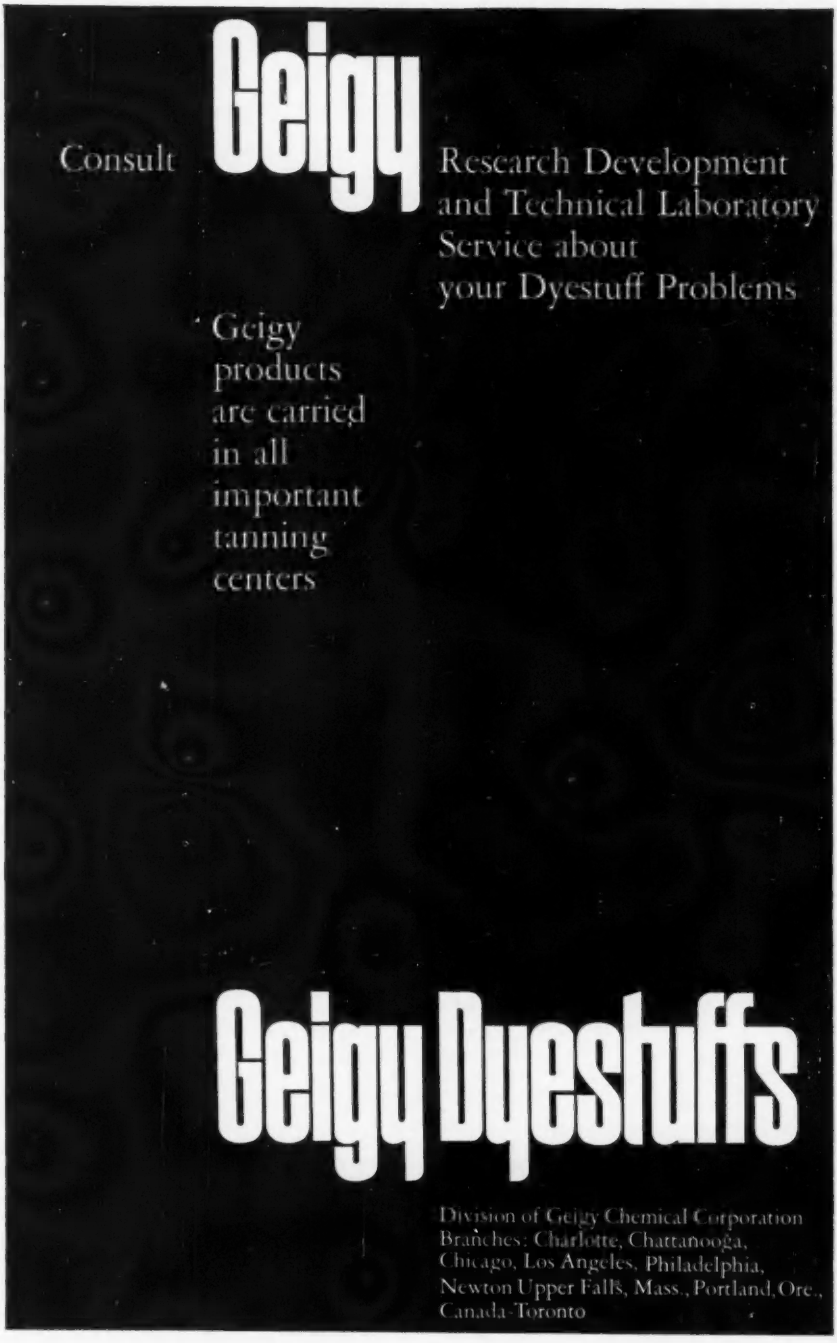
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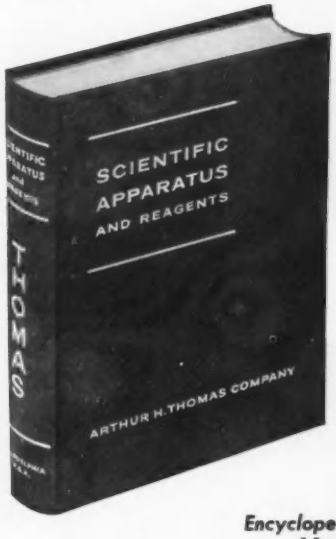

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PRELIMINARY STUDIES OF THE DYNAMIC MECHANICAL PROPERTIES OF LEATHER*

LEE P. WITNAUER AND WILLIAM E. PALM

Eastern Regional Research Laboratory†
Philadelphia 18, Pennsylvania

ABSTRACT

A forced-vibration resonance method was employed for the first time in studying the dynamic mechanical properties of leather. The response of the free end of a reed-shaped leather specimen that was excited by a sinusoidal displacement at the clamped end was determined. Unsymmetrical resonance curves were obtained, indicating a nonlinearity in dynamic mechanical behavior. It is proposed that this nonlinearity was produced by the fibrous network structure of the leather.

INTRODUCTION

Recently, dynamic mechanical test methods have been utilized with considerable success in relating over-all macroscopic behavior to molecular structure in a wide variety of polymeric systems (1). Little information from this type of test is available for leather (2). Although it is difficult to predict the value of such information, certainly the knowledge gained should contribute to a better understanding of the rather complex system of leather.

Various dynamic test methods have been developed to evaluate the mechanical behavior of polymers over a wide range of speeds, from almost static to megacycles per second. Briefly, the dynamic test methods can roughly be divided into three classes: attenuation methods, resonance methods, and direct stress-strain methods (1). Included in the first class is the wave propagation method employed by Kanagy and Robinson in their studies on leather (1). The frequencies employed in this study varied with the specimen but were in the range of 3000–4000 cycles/second. The results that are to be presented herein were obtained by a method included in the second class, a resonance method which utilized relatively low frequencies from a few cycles to a few hundred cycles per second. Since this method

*Presented at the Fifty-sixth Annual Meeting of the ALCA, Lake Placid, New York, June 19–22, 1960.

†Eastern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

has not been previously described in the leather literature, a brief description of the principles involved will be presented.

In the forced-vibration resonance method the mechanical response of a material is measured as a function of applied driving frequency in the vicinity of its natural resonance frequency. Every material so driven has a specific frequency called the resonance frequency at which it undergoes free vibrations, that is, vibrates with a maximum amplitude. At frequencies immediately above and below the resonance frequency the amplitude of vibration decreases. For a linear system the amplitude-of-vibration versus frequency plot is symmetrical, as shown in Fig. 1. The resonance frequency is desig-

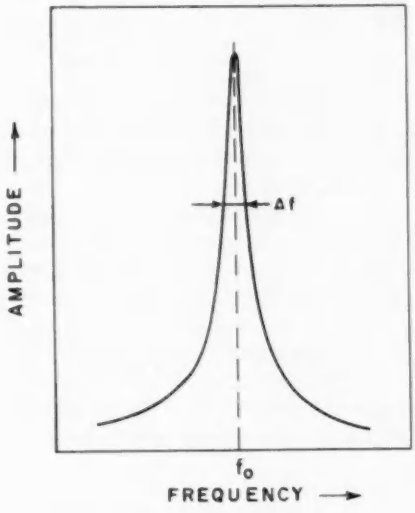

FIGURE 1.—Amplitude-frequency curve for a linear-response material.

nated f_o, the band width Δf. An analysis of this response curve is required to arrive at the dynamic mechanical properties of the material under investigation. The type of analysis needed depends upon the technique employed.

In the present study, the vibrating reed technique was used. The method consists essentially of a determination of the motion of the free end of a cantilever specimen that is excited by a small sinusoidal displacement at the clamped end. Equations have been derived (3) that relate the resonance frequency and band width of the frequency curve to the real and imaginary

parts of the dynamic modulus of the material. The real part of the dynamic Young's modulus, E, can be calculated using the following expression:

$$E = \frac{48\ \pi^2\ d\ l^4}{a_o^4\quad t^2} f_o^2$$

where d is the bulk density of the specimen, l is length, t is thickness, f_o is the resonance frequency, and a_o is a constant associated with the mode of vibration. For the fundamental vibration $a_o = 1.875$.

The imaginary part of the modulus is associated with internal resistance or friction encountered during dynamic deformation. The internal resistance, η, can be calculated from the relation

$$\eta = \frac{48\ \pi^2\ d\ l^4}{a_o^4\quad t^2} \triangle f$$

where d, l, a_o, and t have the same significance as given above and $\triangle f$ is the band width or difference between the two frequencies for which the amplitude has 0.707 times its maximum value.

The mechanical response of leather is probably dependent on at least two factors: (*a*) the viscoelastic properties of the individual fibers, and (*b*) the character of the network structure that exists as a result of fiber-to-fiber interactions. Therefore it would be desirable to be able to establish a relationship which could account for both effects. Perhaps the proper interpretation of dynamic mechanical test data would provide a means of attaining this goal. In addition, the same information might be of value in establishing a basis for setting up a nondestructive test method for use on whole hides and skins. The work that is being reported was undertaken from these points of view.

EXPERIMENTAL

The vibrating reed apparatus used in the study of the dynamic behavior of leather is schematically illustrated in Fig. 2. It consists of a variable oscillator (Hewlett-Packard 202 CD*) which is capable of generating signals of various strength in the frequency range of 5–600,000 cycles/second. To increase the strength of signal beyond that attainable from the oscillator an amplification system (McGowan Model M-60, 60 watts) is used. The signal is subsequently put into the voice coil of a loudspeaker driver unit (Atlas Sound Corp. Model PD-8VL). An aluminum push rod is connected to the driver unit and transmits sinusoidal motion to a sample clamped at its other end. The amplitude of the free end is measured with a traveling micrometer

*The mention of trade products and firms does not imply their indorsement by the United States Department of Agriculture over similar products or firms not mentioned.

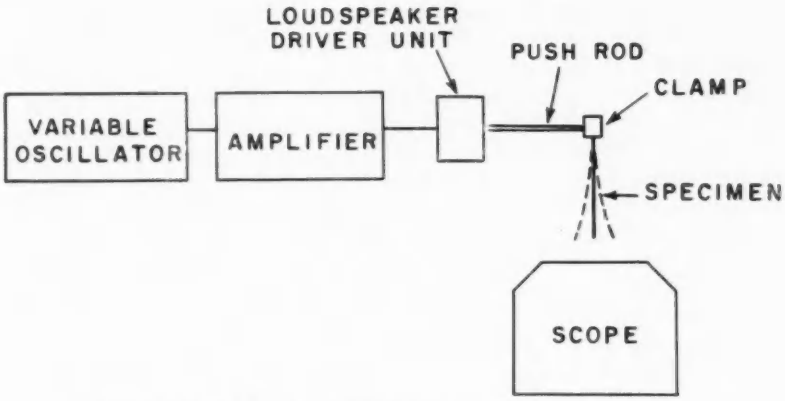

FIGURE 2.—Schematic Illustration of the vibrating reed apparatus.

to ± .01 mm. by observing a magnified image of the vibrating specimen with a 4-power scope.

The data reported herein were obtained using commercially available light leathers. The bulk of the measurements were made on a vegetable-tanned, unfinished calfskin. Specimens used were taken parallel to the backbone in the bend section of the skin. Test specimens were cut so as to have a width of 1 cm. A length of 5 cm. was chosen for making this preliminary study. The natural thickness of the various leather specimens ranged from 0.1 to 0.3 cm.

The measurements were carried out at 73° F. and 50% relative humidity. All specimens were equilibrated at these conditions at least two weeks prior to testing.

RESULTS AND DISCUSSION

Shown in Fig. 3 is the observed amplitude-frequency curve for a vegetable-tanned, unfinished calf. The driving force applied to the specimen at its clamped end was held constant over the employed frequency range, 12 to 25 cycles/sec. The specimen showed a resonance frequency of 16.4 cycles/sec. Particular note of the shape of the response curve should be made. It is not symmetrical. As previously mentioned, the response curve should be essentially symmetrical about the resonance frequency for a linear system. Included in Fig. 3 is the calculated (4) response curve for a linear system with the same resonance frequency and internal resistance. Thus it is quite apparent that under the test conditions employed, the leather specimen exhibited the characteristics of a nonlinear system. Adjacent test specimens of the same skin also produced asymmetric curves.

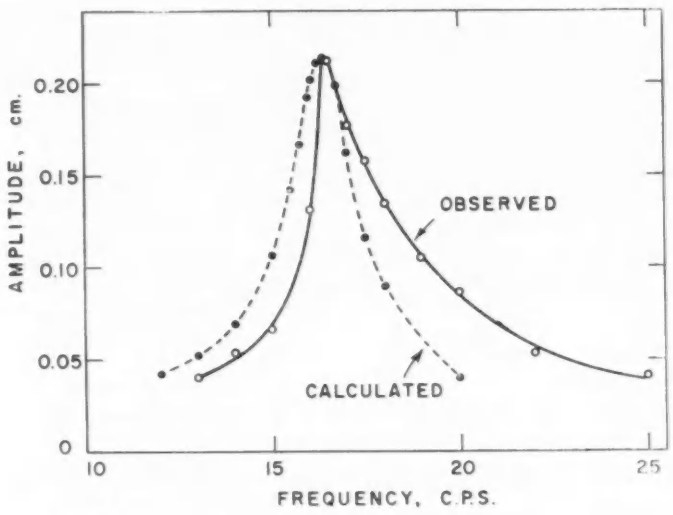

FIGURE 3.—Amplitude-frequency curve of vegetable-tanned unfinished calf.

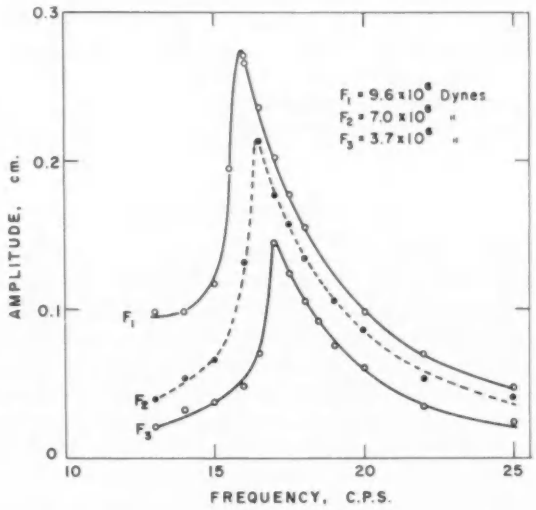

FIGURE 4.—Curves for vegetable-tanned unfinished calf at three different driving forces.

In order to determine whether nonlinearity in dynamic properties was associated with the particular tanned leather studied or was a general characteristic of leather, a number of commercial leathers containing various types and combinations of tanning agents were investigated under similar test conditions. These leathers included vegetable-tanned–chrome-retanned finished calf, chrome-tanned–vegetable-retanned unfinished kip, chrome-tanned–resorcinol-formaldehyde-retanned side leather, and dialdehyde starch-tanned finished calf. The amplitude-frequency curves of all these leathers were asymmetric. However, the curves differed in such details as resonance frequency, amplitude, and band width. A specimen of untanned, acetone-dehydrated calfskin also exhibited nonlinear behavior. Apparently the nonlinearity of the dynamic properties was a characteristic of the system.

A study of the effect of the driving force on the resonance curve was made. Shown in Fig. 4 are the curves for a vegetable-tanned, unfinished leather specimen that were obtained at three different driving forces, $F_1 > F_2 > F_3$. The values of F_1, F_2, and F_3 were 9.6×10^6, 7.0×10^6 and 3.7×10^6 dynes, respectively. The amplitude of vibration at resonance increased with increasing driving force. However, the frequency at which resonance occurred decreased with increasing driving force. If leather were a linear system, the amplitude of vibration would have increased as observed, but the resonance frequency would have remained unchanged. Thus, within the driving force range studied, the leather specimen showed a nonlinearity in dynamic behavior.

The formula previously given for calculating the dynamic bulk modulus of a vibrating specimen showed that the modulus is directly proportional to the square of the resonance frequency. Given in Table I are the calculated

TABLE I

DYNAMIC PROPERTIES OF VEGETABLE-TANNED LEATHER

Driving Force, dynes $\times 10^{-6}$	Dynamic Bulk Modulus, dynes/cm$^{-2} \times 10^{-8}$	Internal Bulk Resistance, dyne/sec/cm$^{-2} \times 10^{-5}$
3.7	2.93	2.4
7.0	2.71	3.2
9.6	2.60	3.6

values for the dynamic bulk modulus and internal resistance at the three driving forces employed. The bulk density of the leather samples was 0.64 as determined from a measurement of weight and volume. The bulk dynamic modulus value increased from 2.60×10^8 dynes/cm^2 for the largest driving force employed to 2.93×10^8 dynes/cm^2 for the smallest. In contrast the apparent internal resistance decreased with decreasing driving force.

An explanation for the observed nonlinearity was sought. It is well known that nonlinearity in mechanical response will result if the elastic limit of the material is exceeded. Perhaps the leather specimens under the particular test conditions employed were being strained, at least in part, beyond elastic limit. Calculations of the maximum strain produced in the vibrating specimen at the maximum amplitude of vibration, that is, at resonance, were made, assuming the specimen to be a uniformly loaded cantilever beam. Maximum strains produced at resonance were found to be relatively small, between 0.2 and 0.8%, for the driving forces used. Such small strains were considered well within the elastic limits of the leather. In addition, the same resonance curve was obtained regardless of the number of times the same specimen had been tested or of the direction of approach to the resonance peak. If the specimen had been permanently strained, duplication of the resonance curve should not have been possible. To insure that some factor had not been overlooked, specimens were mechanically conditioned by cyclic loading and tested. These conditioned specimens produced the same type of distorted resonance curves. Therefore, the observed behavior could not be attributed to a nonlinearity of the ordinary stress-strain characteristics of leather.

What other structural characteristic of leather could effect its dynamic mechanical response? Modifications produced within the fibrous network of hide or skin are known to have a marked effect on the mechanical properties of the leather produced. Could the fibrous network be responsible in some manner for the observed behavior? In any one piece of leather there is undoubtedly a large number of fiber-to-fiber interactions. Some of these fiber-to-fiber contacts are probably of such a nature that they are easily altered. Therefore, the number and extent of such contacts might be expected to change with the amplitude of vibration. This would explain the observed nonlinear dynamic behavior of the leather specimens, since a different system of fiber interactions would be produced for each amplitude of vibration.

This distortion of the resonance peaks has been observed for filled rubber compounds. Gehman (5) in a review on the dynamic properties of elastomers points out that the nonlinearity associated with filled rubber compounds has been described as a thixotropic breakdown of the filler structure. The explanation proposed for the behavior of leather is analogous to that proposed for filled rubber. One basic difference between the two systems is the absence of a measurable hysteresis effect in the leather system. Apparently the time required for reforming the original fiber network in leather is relatively short.

If nonlinearity is due to continuously changeable fiber interactions, then it should be possible to cause the specimen to vibrate at such a low amplitude that essentially no fiber interactions would be altered. The specimen would move as a unit and exhibit the characteristics of a linear system. Ap-

parently the dynamic measurements previously discussed were made at too large an amplitude of vibration or strain. Unfortunately, the experimental setup used was not particularly suited for quantitative determination of a complete resonance curve for small amplitudes of vibration. However, it was possible to measure the resonance frequency and amplitude of vibration at resonance for very small driving forces. A series of measurements were made on the same specimen over a relatively large range of driving forces. The bulk dynamic modulus and corresponding maximum percent strain of the specimen were calculated from the data and are given in Fig. 5. The dynamic

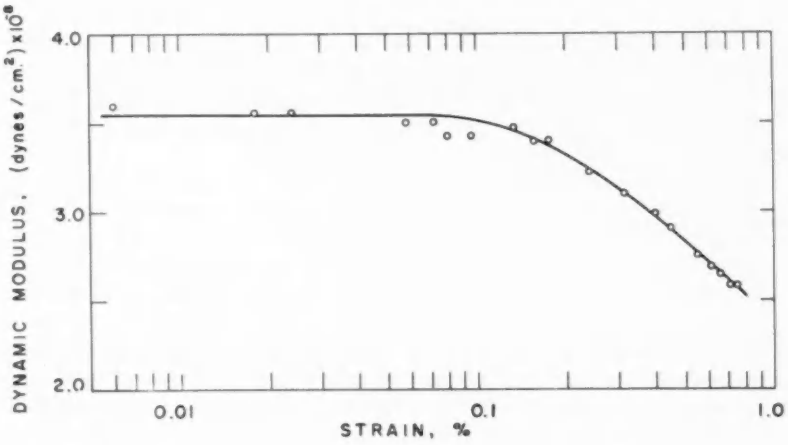

FIGURE 5.—Dynamic modulus-strain curve of vegetable-tanned leather.

modulus increased as the amplitude of the dynamic strain decreased until a strain of approximately 0.1% was reached. Below this strain the dynamic modulus was independent of the strain, indicating that the dynamic behavior of the specimen was essentially linear; practically no change in fiber interactions was produced. The limiting dynamic bulk modulus value obtained from the linear range was about 3.6×10^8 dynes/cm.^{2} This compared favorably with the static modulus, 3.7×10^8 dynes/cm^2, of the same specimen which was measured to torsion.

CONCLUSION

These preliminary results indicate that the forced-vibration resonance method provides a means of obtaining information about the fibrous network structure of leather. Since the type, extent, and number of fiber-to-fiber interactions are altered by chemical modification, fatliquoring, and mechan-

ical working and vary with position in the skin, the potentialities of this dynamic method appear to be great. Many more experimental data are needed, however, before the ultimate value of such studies can be definitely established.

ACKNOWLEDGMENT

The authors wish to thank H. J. Scherr for assembling the vibrating reed apparatus.

REFERENCES

1. Abolafia, O. R. *Survey of the Methods Used to Determine the Dynamic Mechanical Properties of Polymers*, U. S. Office of Technical Services Report PB 121767 (1954).
2. Kanagy, J. R. and Robinson, M. *JALCA*, **51**, 174 (1956).
3. Horio, M. and Onogi, S. *J. Appl. Phys.*, **22**, 977 (1951); Nolle, A. W. *J. Appl. Phys.*, **19**, 753 (1948).
4. Payne, A. R. *Rubber Chem. and Technol.*, **30**, 218 (1957).
5. Gehman, S. D. *Ibid.*, 1202 (1957).

Received October 19, 1960.

DISCUSSION

PROFESSOR WILLIAM T. RODDY: As Dr. Witnauer has pointed out to us, we now have three different methods of measuring the mechanical properties of leather, namely, the attenuation method reported to our Association in 1955 by Dr. Kanagy, the present method which Dr. Witnauer presented to us today, and finally the stress-strain methods of measuring these properties of leather which have been reported over the years.

Our interest in the present work is the nonlinearity of response exhibited in leather by this particular testing method.

When stress-strain methods are used, they will tend to indicate that leather behaves like other polymeric substances, in that it will give good linear response.

The reasons for these differences might be explained to us today by Dr. Witnauer, if he would care to make a few comments.

DR. WITNAUER: I think that in the direct stress-strain measurement the specimen is being subjected to a different type of mechanical action from the one that I described today. In the vibration method, as the sample swings back and forth, the fibers of leather actually make and break contact with one another. When motion stops, the fibers of the network return essentially

to their original positions. This is time-dependent. If the time interval of the measurements were chosen correctly, you could show this behavior by other tests as well.

PROFESSOR RODDY: Where you use the Tinius-Olsen test, for example, and put a load on the grain and flesh side, and gradually increase the load and then release it, you tend again to get curves that are more linear in character than those obtained by this method.

I would like to ask Dr. Witnauer whether it makes any difference whether the leather in this method is bent grain in or grain out.

DR. WITNAUER: No. We have measured the response with the grain in both directions and observed the same response. In a number of specimens the grain layer was removed, and the specimen still gave the same type of response.

PROFESSOR RODDY: Another point made by Dr. Witnauer is that if you compressed the leather up to a given point and then mechanically between your fingers—or any other way—released this compression and then in turn remeasured the leather, it was found that it behaved much as it would if the compression had not been placed on it. I think we have a similar type of response in the way of stress-strain measurements. As an example, if we do not extend the compressed leather up to anywhere near its breaking load, we shall find that it tends to show little or no permanent fiber change. On the other hand, if we do put too much weight on the specimen and bring it up near its breaking load, then it will no longer respond as it would if it had not been compressed.

Dr. Witnauer has expressed to you that the work is very preliminary and that at the present time he does not have any correlation of this test method with the mechanical properties of leather as they might be used in actual service.

The primacy of the spiritual and social well-being of man has always been the measure of nobility. Man's conviction in the loftiness of this purpose has been repeatedly demonstrated through charitable sacrifices and bloody martyrdoms. It takes a devilish depraving of man's goodness to rationalize this ingrained voice of conscience into an incidental happenstance. In these times of insecurity in the wisdom of our intelligentsia, there needs to be a reappraisal of the doctrine of "Science for science's sake" and its twin, "Knowledge for knowledge's sake." Should science be regarded as merely amusement for the erudite few? Should it be a floating iceberg of drifting data? Or should it be a means of infusing man's perceptions into his feelings for his fellows and his consciousness of life?

—R. G. H. Siu, *The Tao of Science*, a joint publication of The Technology Press of M.I.T. and Wiley, 1957. © Massachusetts Institute of Technology.

ELASTASE ACTIVITY OF SOME ENZYMES AS RELATED TO THEIR DEPILATORY ACTION*

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ABSTRACT

The elastase activity of some 15 enzyme preparations has been determined by three methods: formol titration, histological, and gravimetric. Results obtained with the three methods did not rate the enzyme preparations in the same order, nor is there any correlation of hair loosening with the elastase activity. A preparation of keratinase from *Streptomyces fradiae* exhibited the most potent elastase activity of any of the enzyme preparations tested.

INTRODUCTION

This laboratory has been working for some time on an enzyme unhairing process that would be rapid and, in addition, would eliminate the problem of disposing of used lime-sulfide liquors, a problem which is becoming increasingly acute. Although considerable information has been obtained (1, 5, 8), the exact nature of the substance that binds the epidermis to the dermis is not known, and hence the identity of the enzyme or enzyme systems that cause the breakdown of this material remains obscure. Such information, if available, would be very useful in establishing an efficient enzyme unhairing system.

We have attempted to throw light on this reaction by assaying enzyme preparations for various activities and trying to correlate such activities with their hair-loosening ability. Earlier, it was shown that no correlation exists with starch-dextrinizing power and that only a casual relationship to casein digestion was demonstrable (1). Among the components of the system which have been suggested as anchoring material for the epidermis is the fibrous protein elastin (2, 3). If a strong correlation between elastase activity and hair-loosening ability could be shown, it would lend credence to this view.

*Presented at the Fifty-sixth Annual Meeting of the American Leather Chemists Association, Lake Placid, New York, June 19–22, 1960.

†Eastern Utilization Research and Development Division, Agricultural Research Service, United States Department of Agriculture.

EXPERIMENTAL

Materials

Hide samples were all from green-salted hides obtained from a local slaughter house. On arrival at the laboratory they were fleshed and stored in a refrigerator in moisture-proof bags.

Enzymes were obtained from commercial sources and were used without further purification. They are listed and described in Table I.

TABLE I

ENZYME PREPARATIONS USED IN ELASTASE ASSAYS

Enzyme and Supplier	Source
Miles Chemical Company, Clifton, N. J.	
HT Proteolytic (extra high potency)	Bacterial
HT Concentrate (market grade)	"
HT Proteolytic 200	"
Special Diastase 160	Plant and Animal Materials
Bromelin	Pineapple
Rohm & Haas, Philadelphia, Pa.	
Protease 15 Concentrate	Bacterial
Rhozyme P11	Fungal
Lipase B	Microbial
Wallerstein, Inc., New York, N. Y.	
Protease 4511-3	Bacterial
Prolase 40	Fungal
Nutritional Biochemicals Corp., Cleveland, Ohio	
Trypsin Non-Crystalline 4 x USP	Pancreas
Papain	Plant
Pabst Laboratories, Milwaukee, Wisconsin	
Protease L-56-D	Bacterial
Viobin Corporation, Monticello, Illinois	
Viokase	Pancreas
Merck Sharp and Dohme, Rahway, New Jersey	
Keratinase	*Streptomyces fradiae*

Elastin for use in the formol titration procedure was that purified from *ligamentum nuchae* obtained from the Worthington Laboratories*.

*Mention of a company and/or product name by the United States Department of Agriculture does not imply approval or recommendation of the company or product to the exclusion of others not mentioned.

Methods

Formol titration method.—This is the standard method for determining carboxyl groups resulting from hydrolysis of the peptide links, by enzymes in this case. Formaldehyde is used to bind the amino groups, and the carboxyl groups are titrated. Elastin was treated with three concentrations of the enzyme at different pH levels for 4 hours at 30°C. on a shaker. After the addition of formaldehyde the solution was titrated with standard alkali. The control was run in the same way except that the enzyme was added after the formaldehyde. Samples were titrated with 0.1*N* NaOH using phenolphthalein indicator.

Histological and gravimetric methods.—Two-inch-square pieces of hide were immersed in 2% enzyme solutions for 7 or 17 hours at 38°C. This concentration is about ten times that required for unhairing. It was selected to make certain that lack of enzyme would not be a limiting factor in periods of one working day, or overnight plus one working day. Control pieces from the same hide were immersed in 5% salt solution until the hair and epidermis could be removed, which required up to 2 weeks. Bacterial growth was prevented by adding 0.015% phenylmercuric acetate to the solutions. The hair and epidermis were removed from all samples, and they were thoroughly washed. Samples for histological assay were fixed in formalin and sectioned, stained, and evaluated as described by Everett *et al.* (4).

For the gravimetric assay the enzyme-treated hide pieces and the controls were autoclaved in 200 ml. of distilled water at 15 lb. pressure for 4 hours to dissolve the collagen. The solutions were decanted through tared, fritted-glass crucibles, and the residues were washed once with hot water. The residues were again autoclaved, transferred to glass crucibles, washed consecutively with ethyl alcohol and acetone to remove the fat, and dried. Results are reported as "percent less than control."

Unhairing activity.—The comparative hair-loosening activity of most of these enzymes has been reported previously (1), and the method of measurement has also been given (1, 5). Essentially it consisted of pulling a 1″ blade repeatedly over the treated hide until no further hair was removed. The number of pulls and the estimated percent of hair removed were recorded. In this paper a numerical value for hair loosening has been obtained by dividing R, the estimated percent of hair removed, by the number of pulls P, multiplied by the enzyme concentration in solution as percent.

RESULTS

Data obtained with several enzymes, at two pH levels in most cases, using the formol titration procedure, are plotted in Fig. 1. The highest values, i.e., the most acid produced, were obtained with a bacterial protease

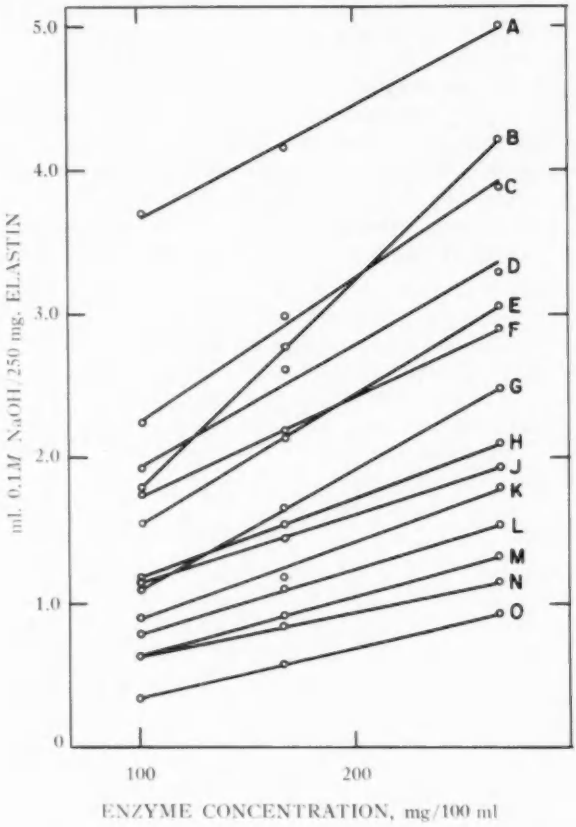

FIGURE 1.—Relationship between enzyme concentration and titratable acid produced from prepared elastin in 4 hours at 30°C.

A.	HT Proteolytic P	pH 6.5
B.	HT Proteolytic P	pH 8.8
C.	HT Concentrate 4903	pH 6.5
D.	Protease 15 Concentrate	pH 6.5
E.	HT Concentrate 4903	pH 8.8
F.	Protease L56-D	pH 6.5
G.	Viokase	pH 8.8
H.	Protease 4511-3	pH 6.5
J.	HT Proteolytic 200	pH 7.0
K.	Trypsin Non-Crystalline	pH 8.8
L.	HT Proteolytic 200	pH 8.8
M.	Viokase	pH 7.0
N.	Viokase	pH 6.5
O.	Rhozyme P11	pH 6.5

at pH 6.5. At pH 8.8 the activity with this enzyme was considerably less, although the slope of the curve was steeper, indicating a decreased pH effect at the higher concentrations of enzyme. All the bacterial proteases were more active at neutrality or slightly below than at pH 8.0 or above. The pancreatic enzymes were more active on the alkaline side, as expected. The two fungal enzymes showed only very weak activity.

The histological procedure permits an evaluation of the general attack on the hide constituents by the enzymes. The effect of pH on general proteolysis, as well as elastolysis, is shown in Table II for the enzyme preparation HT Proteolytic. Controls without enzyme were run concurrently, but only

TABLE II

EFFECT OF pH ON ELASTOLYSIS AND GENERAL PROTEOLYSIS OF HIDE BY HT CONCENTRATE 4903

(*2% Solution, 7 hr., 38°C.*)

pH	Elastolysis		General Proteolysis*	Condition of Epidermis
	Elastin Degraded %	Completely Cleared %		
4	0–10	0	weak	separated
5	10–25	0	weak	separated
6	20–40	0	moderate	mostly gone
7	50–75	10–20	strong	gone
8	40–60	0–10	strong to severe	gone
9	40–60	10–20	strong	gone
10	30–50	0	strong to severe	gone

*Attack on cells, glands, muscle fibers, etc.

very mild action at the pH extremes was observed. With HT Proteolytic, the strongest attack on elastin was at pH 7.0, but strong action continued even at 10.0. It is interesting that complete elimination of elastin occurred to a depth of only 20% of the papillary layer and then only at the pH of maximum activity. General proteolysis, observed as attack on glands, muscles, capillaries, etc., was strongest at pH 8.0 and above. The epidermis was separated from the dermis even at pH 4.0. The epidermis was almost completely disintegrated at pH 6.0 and disappeared completely at pH values above this point.

Results obtained with 14 enzyme preparations using the three different methods of assay are compared in Table III. Also included are results of the unhairing activity of these enzyme preparations. According to the formol titration procedure, the top-ranking preparations are of bacterial origin. Bromelin also ranks high by this method. In the histological method, Vio-

TABLE III

RELATION OF THE ELASTASE ACTIVITY TO HAIR-LOOSENING ACTION OF 14 ENZYME PREPARATIONS

	Elastase Assay Method									Hair Loosening*				
	Formol Titration			Histological			Gravimetric							
Enzyme	pH	Meq-N/g.†	Rank	‖Incubation Time	Elastin Degraded %	Rank	pH‡	Percent Less Than Control	Rank	Enzyme Concentration %	P**	R††	(R/P)x Concn.	Rank
HT Proteolytic P	6.5	12.5	1	7	75–100	2	6.7	79.0	3	0.06	2	99	825	1
HT Concentrate	6.5	9.8	2	7	50–75	4	6.6	70.5	5	0.10	3	99	330	2
Protease 15 Concentrate	6.5	8.3	3	17	30–50	13	6.3	70.0	6	0.12	6	90	125	5
Protease L—56—D	6.5	7.3	4	17	30–50	13	6.1	49.0	12	0.15	3	99	220	3
Bromelin	5.2	7.0‡‡	5	7	60–80	3	5.1‡‡	53.5	10	0.41	3	98	79	8
	8.8	none												
	5.5	none		7	50–70	5	7.4	70.0	6					
Viokase	8.8	6.3	6	7	80–100	1	8.6	74.0	4	0.38	10	95	22	11
	6.5	2.9		7	60–80	3	7.3	83.0	2					
	5.5	none		7	30–50	8	5.7	55.5	9					
HT Proteolytic 200	7.0	5.0	7	7	10–30	11	6.7			0.21	3	95	151	4
Protease 4511—3	6.5	5.0	7	17	70–90	12	6.4	51.5	11	0.37	3	98	88	7
Trypsin (4 x USP Pancreatin)	8.8	4.5	8	7	50–70	5	8.7	88.0	1	0.26	3	95	122	6
				7	30–50	8	7.4	67.5	7					
				7	20–40	10	5.8	38.0	15					
Papain	8.8	3.5***	9	7	30–40	9	7.3	6.5	19	0.73	6	97	22	11
	5.5	none		7	40–70	6	5.5	33.0	16					
				7	50–60	7	5.2‡‡	57.0	8					
Rhozyme P-11	6.5	2.3	10	17	20–30	14	6.4	39.0	14	0.78	3	98	42	9
Prolase 40	5.5	1.0	11	17	0–5	16	5.9	44.0	13	0.83	4	98	30	10
Special Diastase 160	6.5	0.0		17	5–20	15	6.1	9.5	18	2.59	2	99	15	12
Lipase B	6.5	0.0		17	0		6.3	28.5	17	10.0	10	0	—	—

*From Cordon *et al.* (1,5).
**Number of pulls with scraper.
***With BAL as activator.

†Enzyme concentration, 0.27%.
††Estimation of percent hair removed.

‡Applies to histological and gravimetric determinations.
‡‡With 1% sodium metabisulfate.

kase at pH 8.6 was most active; a bacterial protease, HT Proteolytic P, was next, and bromelin and Viokase (pH 7.3) were tied for the third position in activity. According to the gravimetric assay, trypsin at pH 8.7 ranked first; Viokase at pH 7.3, second; and HT Proteolytic P, third.

Bromelin showed no activity by the formol titration procedure unless an activator such as sodium metabisulfite was present. This reducing agent also increased the activity of bromelin in the histological assay.

Papain was not active according to the formol titration assay even in the presence of sodium metabisulfite, but 2,3-dimercaptopropanol (BAL) produced considerable activation.

Rhozyme P11 and Prolase 40, two fungal enzymes, and special Diastase 160, which is a mixture of plant and animal enzymes, were among the weakest in all the materials assayed. Lipase B showed activity only in the gravimetric assay, and this was very weak.

Since the completion of this work with these enzymes another enzyme preparation possessing strong depilatory activity has become available. It is produced by *Streptomyces fradiae* and was discovered, and named keratinase, by Nickerson and Noval (6, 7). It is now under commercial development. Since the work with this enzyme was, of necessity, carried out on a different hide, the results are reported separately.

As with the other enzymes, a high concentration, roughly ten times that needed for unhairing, was used to insure that the amount of enzyme would not be a limiting factor and that activity would be evident in a short incubation period. The strength of this enzyme has been determined by an assay procedure in which wool is used as the substrate, and absorption in the supernatant at 280 mμ is measured (7, 8). The same assay procedure has been used in this work. About 100 to 150 keratinase units per ml. of solution are

TABLE IV

ELASTASE ACTIVITY OF KERATINASE FROM *STREPTOMYCES FRADIAE*

Concentration Ku/ml	Time hr.	pH	Additive %	Histological		Gravimetric
				Depth Degraded %	Depth Cleared %	Percent Less Than Control
1500	7	6.8	none	75	45	56
1500	7	8.8	Borax, 0.5	100	100	84
1500	7	8.7	Borax, 0.5 NaCl, 5.0	60	35	85
136	22	8.7	Borax, 0.5	100	100*	
136	22	8.5	Borax, 0.5 NaCl, 5.0	100	100**	

*No elastin in entire thickness of hide
**Many fragments in center corium

required for good depilatory action. Accordingly, 1500 units per ml. were used in this study. Table IV gives the results obtained with the three assay methods when the pH was left unadjusted (pH 6.8), with borax added to raise the pH to 8.8 (approximately the optimum for unhairing action), and with 5% sodium chloride present in addition to the borax. Strong elastase activity was evident even at the low pH of 6.8 and was very strong at 8.8. The effect of sodium chloride in the enzyme solution was tested because it appears to have a beneficial effect on the physical characteristics of the hide and possibly of leather made from it. As shown, it decreased the elastase activity, as measured histologically, but the elastin was affected in some manner because it was hydrolyzed by the hot water in the gravimetric determination. Elastase activity was determined histologically on some bends which had been treated with keratinase at 136 K units/ml. in a rocker vat for 22 hours at 40°C. Without salt in the enzyme solution there was no trace of elastin remaining throughout the entire cross section of the hide. This is the only time we have observed such complete removal of elastin. With sodium chloride present, many fragments of elastin still remained in the center of the corium, but the grain and flesh areas were completely cleaned out.

TABLE V

ELASTASE ACTIVITY OF HT PROTEOLYTIC E 210 IN THE PRESENCE AND ABSENCE OF SODIUM CHLORIDE

Concentration %	Time hr.	pH	Additive %	Histological		Gravimetric
				Depth Degraded %	Depth Cleared %	Percent Less Than Control
2.0	7	6.6	none	40	13	53
2.0	7	8.7	Borax, 0.5	55	15	49
2.0	7	8.8	Borax, 0.5 NaCl, 5.0	18	0	61

Sodium chloride was shown to exert a similar effect on the elastase activity of the bacterial protease HT Proteolytic, Table V. From Table V it appears that the elastase activity of this enzyme was inhibited by salt when measured histologically but was unchanged when measured gravimetrically.

From the data for hair loosening, it is seen that of the seven most active preparations, six are of bacterial origin. (Although not included in this comparison for reasons stated above, keratinase is also a very potent hair-loosening agent). The elastase assay most nearly agreeing with this ranking is the formol titration, but bromelin and Viokase are included in place of two of the bacterial preparations, and only the first two agree as to order. Certainly no good correlation exists between hair loosening and any of the assays. Furthermore, the assays do not agree with each other.

DISCUSSION

As far as is known, the use of the formol titration procedure for determining elastase activity has not been successfully employed before. Banga, in an attempt to measure pancreatic elastase activity, is reported by Thomas and Partridge (9) to have been unable to detect the release of amino groups by this method. This method has the advantage over several others in that it is direct and measures actual breakdown of tissue, i.e., rupture of peptide bonds. The splitting of dye molecules from stained elastin as in the method of Sachar *et al.* (10) might not be indicative of elastin breakdown unless supported by other data. Any method utilizing isolated elastin suffers from the fact that the elastin is undoubtedly changed by the isolation procedure. In this respect the gravimetric method used, or a very similar one employed by Ornes and Roddy (11), is superior. However, the difficulty of obtaining suitable controls with the notoriously nonuniform hide is objectionable. Furthermore, any method which measures the unidentified residue of a reaction is open to the criticism that the residue may not consist wholly of the constituent in question. In this case keratin, fat, etc. may not be completely removed.

Histological studies are certainly of great value, but interpretation of results must be made with caution. It was found that the elastin in lime-sulfide unhaired hide was stained in almost characteristic manner with elastin stains. However, the elastin had been attacked, as shown by the fact that when this limed hide was autoclaved, about half of the elastin was dissolved. Banga *et al.* (12) have reported an analogous situation. The transparency of elastin particles increased through enzyme action, although dissolution of elastin could not be demonstrated until later.

The use of intact tissue for elastase assay has the advantage that the elastin is not altered by preparatory procedures. It appears, however, that other components of the hide influence the enzyme action. Neither bromelin nor papain showed any activity on isolated elastin without an activator, whereas on intact hide there was considerable action without addition of activators.

Although some of the best depilatory enzymes were also high in elastase, no high degree of correlation between these two actions could be demonstrated. The results indicate that elastin does not contribute to the anchoring of the epidermis. Therefore, measurement of elastase activity would not be of any assistance in determining the unhairing action of enzymes.

SUMMARY

Three methods of determining elastase activity have been described. Elastin activity on isolated ligament was measured by a formol titration procedure. Gravimetric and histological methods were used on intact hide. Agreement among the three methods was not good. Elastase activity of the

enzymes did not correlate well with their depilatory action. Keratinase from *Streptomyces fradiae* shows the strongest elastase activity of any of the enzymes tested.

REFERENCES

1. Cordon, T. C., Jones, H. W., Clarke, I. D., and Naghski, J. J. *Appl. Microbiol.*, **6**, 293 (1958).
2. Szodoray, L. *Archives of Dermatology and Syphiology*, **23**, 920 (1931).
3. Medawar, P. B. *Quart. J. Micro. Sci.*, **94**, 481 (1953).
4. Everett, A. L., Cordon, T. C., Kravitz, E., and Naghski, J. *Stain Technol.*, **34**, 325 (1959).
5. Cordon, T. C., Windus, W., Clarke, I. D., and Naghski, J. *JALCA*, **54**, 122 (1959).
6. Noval, Joseph J., and Nickerson, Walter J. *Bact. Proc.*, p. 125 (1956).
7. ———, *The Decomposition of Keratin by Microorganisms*. Thesis, Rutgers University, The State University of New Jersey, 1957. Microfilms, Inc., Ann Arbor, Mich.
8. Everett, A. L. and Cordon, T. C. (In preparation)
9. Thomas, J. and Partridge, S. M. *Biochem. J.*, **74**, 600 (1960).
10. Sachar, Leo A., Winter, Kathleen K., Sicher, Nelle, and Frankel, Sam. *Proc. Soc. Expt. Biol. and Med.*, **90**, 323 (1955).
11. Ornes, C. L. and Roddy, W. T. *JALCA*, **55**, 124 (1960).
12. Banga, Ilona, Baló, J. and Horváth, Magdolna. *Biochem. J.*, **71**, 544 (1959).

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DISCUSSION

Dr. James Constantin (Merck and Company): We are again indebted to Dr. Cordon and his associates at the Eastern Regional Research Laboratory for another fine paper on the methods and measurements of enzymatic unhairing.

In my opinion Dr. Merrill, I think in "The Chemistry and Technology of Leather", states the problem of enzymatic unhairing fairly when he says that we must know how enzyme X acts on substrate Y, forming product Z.

As to the question of enzyme X we can identify it by a number of assay methods. Over the last few years, Dr. Cordon's work on the effect of various enzymes on substrate Y has been most interesting.

Dr. Cordon, you have mentioned in the course of your discussion starch dextrinization, gelatin viscosity, and casein hydrolysis as measures of protease activity. Can you elaborate on other methods that you have used in your search for a method of enzyme unhairing?

Dr. Cordon: We have investigated their action on gelatin. We find hair-loosening activity associated with strong proteolytic enzyme. But we do not find a high correlation between depilatory action and gelatinase activity by any of the three procedures we have used.

DR. CONSTANTIN: In a meeting of the Society of American Bacteriologists in May, Dr. Cordon, you also mentioned the keratinase assay of Noval and Nickerson, and if it were reported to me correctly, you found a fairly good correlation between enzyme activity and this keratinase assay. But once again it was the same type of correlation, wasn't it?

DR. CORDON: Yes. That is true. We have not compared the depilatory action with the keratinase activity. But I understand you have, and I know Dr. Nickerson claims that he has followed it. I am sure this assay would not be applicable to other enzymes. We have tested bacterial enzymes by the keratinase assay, and although they are strong depilatories, they have very little action on the wool, according to this procedure.

DR. CONSTANTIN: From reading some of your other papers, and from a quick comparison of the 2% level of enzyme that you mentioned, and also considering the somewhat higher temperatures used (40°), we know as a rule of thumb that enzyme activity will roughly double for every 10° C. rise in temperature. Actually then, doesn't this mean that the level of enzyme that you used in these elastinase experiments is something like twenty times the level that you need for effective unhairing?

DR. CORDON: Yes, I think that is correct. As I mentioned in the paper, we were not interested in unhairing in this case. We wanted to measure the effect these enzymes had on the elastin, and we wanted to produce the effect in one day without having to come back to the laboratory in the middle of the night. We put enough enzyme in so that the reaction would be fairly advanced in seven hours or, if not, so that observations could be made in 17 hours.

DR. TURLEY: I am not surprised that you find no correlation between the elastase activity and depilation. I wonder where the idea came from that the elastin fibers might be penetrating into the epidermis. In all the classic pictures of skin on the bodies of animals, it always seems that the elastin is anchored within the corium itself. I did not see it in your pictures, but if you go to the edge of the epidermis and the grain membranes, you will find elastin fibers growing smaller and smaller, but never do they seem to penetrate into the epidermis. So I am not surprised to find no correlation between elastase activity and depilation.

DR. CORDON: I found two references in medical literature in which it was claimed that elastin does play a role in anchoring the epidermis to the dermis, but our results do not point to that conclusion.

DR. BUECHLER: In your histological studies, Dr. Cordon, you measured the depth of penetration of the enzymes from the grain surface. Did you also find any evidence of penetration through the sides of the hair follicles?

DR. CORDON: That would be very difficult to determine. As I mentioned, fragmentation of the elastin fibers occurs first. Complete clearing out as the enzyme penetration progresses does not take place. First, voids appear in the fibers, and then just fragments are left. I believe, however, that the enzyme does penetrate through the hair follicles.

Education should also stress factualizing and humanizing of events. Scientists must see themselves as they are. They are just men and women driven by the same temptations, susceptible to the same prejudices, and committing the same errors as the citizens of the pre-science centuries and the laymen of modern times. The annals of science need not be censored and warped to picture scientists as steely paragons of rational virtues. It is not degrading to admit that Copernicus did not have enough data on which to draw valid conclusions, that Kepler relied on the horoscope, that Bacon was frequently mean, that Faraday worked on false theories, that Darwin made lots of mistakes, that Newton was peevish and engaged in petty maneuvers to detract credit from Hooke and Leibniz, that Dickens and Balzac wrote for money or that Sir Robert Walpole and Daniel Webster dealt occasionally in blatant venalities. To recognize their frailties is merely to understand that beneath the scientific and artistic personalities lies the same human protoplasm. Their behavior in private life is not the aspect of their personality which acts on our scientific knowledge through their works. Neither is the perfection of their professional efforts any index of the excellence of their human selves.

. . . . . .

Wiser scientists are beginning to realize that a specialist is but an abstraction of man, a personality out of context. They are beginning to appreciate Toynbee's conclusions that "there is no correlation between progress in technique and progress in civilization." Their souls clamor in their native humility for a return to the complete man. Yet to be men as men, they must cease being a particular kind of men. They cannot be men as scientists. They must shake off their servitude to the chains of abstracted and rational thought. They must control the scientific implements, put them in their proper perspective and lose them in the intimacy of their total experience as men.

Life flowed on quite well before science matured into her modern form . . . But modern science is an ingredient which can add new zest to life. The task before us is to emulsify this component into the older and profounder art of life.

—R. G. H. Siu, *The Tao of Science*, a joint publication of The Technology Press of M.I.T. and Wiley, 1957. © Massachusetts Institute of Technology.

ANALYSIS OF RAW HIDES AND OF HIDES IN PROCESS

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ABSTRACT

Estimations of moisture, fat, hide substance, pH, ash, total alkalinity, free causticity, and chlorides are of substantial importance in controlling the condition of raw hides and the procedures taking place in soaking, liming, bating, pickling, and tanning operations. Nevertheless, methods serving these purposes occur rather seldom in the literature, and they all are connected with serious difficulties.

It was found that by slow, gentle heating, specimens taken from hides in storage or in different stages of process may be brought to a uniform condition in which all determinations may be carried out with great accuracy and reliability. Some of the methods found in the literature could be applied without alteration at this stage; some of them had to be modified in order to serve the purpose with best efficiency.

INTRODUCTION

Among all the values which may be determined in raw or processed hides, moisture is of fundamental importance. It indicates the condition and the commercial value of raw hides, the grade of rehydration in soaking, of swelling in lime, of falling in the bate and in the pickle, the dehydrating or swelling action of tannage, and the effects of wringing, setting, drying, and sammying operations. At the same time it is indispensable for relating all other findings to the same basis.

The most generally adopted form of moisture determination is simple drying as specified by the ALCA (1). Objections were raised against this method for a long time (8), mainly because fats may oxidize and certain chemicals may volatilize by heat (17). However, R. Lauffmann (12) and A. Küntzel (13) objected to fat extraction before moisture determination, and there is no doubt that this method is too awkward to yield accurate results. Procter (8) has pointed out that other substances besides fats may

decompose too, and therefore extraction does not solve the problem. Procter advocated the application of vacuum (10) and of an inert gas atmosphere (8) in order to avoid these troublesome influences, but these suggestions never became popular, probably because they were not simple enough for routine work.

Determination of moisture by drying at 100°C. may be carried out properly only if the substance is disintegrated and offers a large surface for evaporation. If this condition is not fulfilled, decomposition will be unavoidable because of too long exposure to heat. This is particularly true for raw, limed, or semitanned hides which curl up badly and form a hard, impermeable crust. On the other hand, if such specimens are disintegrated, their moisture content undergoes substantial changes.

The same phenomena of curling and crust formation occur to an even greater extent if a moisture balance with infrared light is applied. This instrument is recommended for grain and other materials of not too large particle size (15, 16), and it is suitable for tanned leather which can be disintegrated quickly and without too many losses, but not for raw or semitanned hides.

Colin-Russ (18) has recommended a gas volumetric method using calcium carbide, but Lauffman (12) did not consider it serviceable, and it was never widely used.

Moisture meters based upon electric conductivity like the KPM type made by P. Mundinger G.m.b.H. in Renningen, Württemberg, cannot be used on any material whose moisture content exceeds 28%, and the fat and electrolyte contents of leather create serious difficulties on the lower level.

Karl Fischer's titration method (19) has not been applied to leather, probably because its highly active ingredients may interact with substances contained in the leather, and because the same problem of disintegration is involved as in drying methods.

Marcusson's distillation method (20, 21) was widely adopted, and Wilson (17) considered it reliable. More recently Küntzel (13) has been very much in its favor, with particular preference for Scholz's modification (22). As a matter of fact, this latter has no advantages when compared to other modifications, and the following objections may be raised against each one of them:

The graduation of the receiver cannot be made fine enough to avoid fairly significant errors in reading. The specimen cannot be made heavier than 5–10 grams, and when cutting such a relatively small piece the pressure of the knife blade influences the moisture content appreciably. Further disintegration would cause substantial changes in the moisture content, and therefore the specimen has to be heated as a whole. At the relatively high boiling points of toluene (111°C.) and xylene (137°–140°C.) the phenomena of curling

and of crust formation are even worse than in drying. The last remnant of water is retained obstinately, and it is hard to determine when the end point is reached because the distillate is always cloudy.

Küntzel (13) indicated that this cloudiness has no further bearing upon the results because it appears in the distillation of fatliquored skins only and it may be cleared by heating. Actually, it was observed that limed and bated hides yielded more cloudiness than fatliquored ones, and although the cloudiness could be cleared by heating, it returned again when the receiver was cooled for reading. The mere existence of this cloudiness proves that some kind of decomposition took place under formation of a volatile substance, jeopardizing the reliability of the method.

Very few methods for the estimation of ash, total alkali, and free causticity could be found in the literature (9, 11, 14). Because they all call for slicing the specimen, it is evident that two moisture determinations are necessary in each case: true moisture on a specimen which had little or no mechanical treatment, and actual moisture on the sliced specimen.

According to Procter (9) free causticity was determined by agitating the sliced specimen in water and titrating it with acid in the presence of phenolphthalein. This titration may last for several hours, and the end point is uncertain.

No method for determination of pH in wet hides could be found. The official method (2) calls for grinding the leather in a Wiley mill (3), which evidently cannot be done with a wet substance. Wet hides may be sliced, but the uniform thickness of the slices and the various amounts of acid or alkaline liquor squeezed out of them cause alterations of pH. The amount of water to be added is also doubtful because the high moisture content of the specimen does not permit applying the proportion 1:5 as specified by ALCA (2). The amount of water added should really depend upon another moisture determination.

For the determination of chlorides a method recommended by Jany (23) could be applied successfully, but this too is dependent upon the actual moisture content, and it is somewhat lengthy for serial determinations.

EXPERIMENTAL

Sampling.—Specimens must be fairly heavy so that percentage error from inaccuracies in weighing will be minimized. Rectangular pieces, 7″ x 3″ or 6½″ x 3½″, weighing about 100 g. were most satisfactory. They have to be cut with a sharp knife, avoiding any pressure upon the surface of the specimen proper. Limed hides and those from a somewhat advanced stage of tannage are firm enough to shed adherent water, and raw hides do not carry any; therefore, they can be weighed immediately. For softer specimens blotting is not satisfactory because it is impossible to exert the same pressure

in each case. It was established on pieces with no adherent water that hanging 6 min. did not change their weights appreciably; therefore, soft specimens with adherent water were left hanging for this time, clamped in the extreme corner. Butts and bends were sampled on the backbone line at a distance of ¼ of the total length from the tail; shoulders, at the crossing of the butt and backbone lines; sides, at the backbone line at a distance of 1/6 of the total length from the tail; bellies, at the center of the butt line.

Preliminary moisture.—A balance of 0.1 g. accuracy is needed. Weigh a predried watch glass, then weigh the specimen, then leave the specimen hanging at room temperature for 24 hr., clamping it the same way as described above. Put the watch glass below the hanging specimen. After 24 hr. put the specimen on the watch glass, flesh upwards, and dry at 52°–55°C. for another 24 hr. Leave the dried specimens in the open air for one day, in order to achieve perfect balance with the humidity of the surrounding air and to prevent changes of weight during the following grinding operation. Then weigh the specimen, and calculate Preliminary Moisture, PM, by dividing the weight loss by the original weight and multiplying by 100.

Preparation for analysis.—After weighing the specimen, break it into pieces, grind, and store in tightly stoppered bottles as requested by ALCA specifications (3).

Moisture.—Determine M', the moisture of the ground specimen, according to ALCA specifications (1).

Calculate M, the moisture of the original specimen, as follows:

$$M = PM + \frac{M'\,(100 - PM)}{100}$$

Fat and hide substance.—Determine both according to ALCA specifications (4, 5), and calculate on original moisture basis as follows:

$$F = \frac{F'\,(100 - M)}{100 - M'}$$

F is the fat content of the original specimen; F' is the fat content found in the ground specimen.

Ash and total alkalinity.—Determine ash according to ALCA specifications (6), and relate it to the original moisture content the same way as the fat content.

Attempts to determine total alkalinity by titration against methyl orange or to pH 3.0 failed entirely, probably because of the interference of the acid-

binding capacity of proteins. Therefore, 0.5*N* acid was added to the ash, treated 30 min. cold and 10 min. at gentle boil, and the excess was back-titrated with 0.5*N* potassium hydroxide with Methyl Purple as indicator. If V' ml. acid of factor f' is added and V'' ml. alkali of factor f'' is used, the total alkalinity TA is calculated as follows:

$$TA = \frac{0.5608\ (V'f' - V''f'')\ (100 - M)}{100 - M'} \text{ percent calcium oxide}$$

pH.—Determine in the ground substance according to ALCA specifications (2). Soak the specimen overnight, and agitate mechanically for 10 min. before measuring pH.

Free causticity.—An attempt to use phenolphthalein as indicator failed; it was impossible to observe the color change accurately, probably because of the influence of proteins in solution. Therefore the sample used for pH determination was titrated to pH 8.0 with 0.5*N* acid. Titration has to be continued until pH does not go back above 8.0 after 5 min. As a rule 30 min. are needed to reach this stage.

If V ml. sulfuric acid of factor f is used, the free causticity FC is calculated as follows:

$$FC = \frac{0.5608\ V f\ (100 - M)}{100 - M'} \text{ percent calcium oxide}$$

Chlorides.—A simplified method has been tried instead of incineration (23). Five grams of the ground specimen were weighed accurately and transferred to a bottle fitting a shaking machine of the rotating type as described for tannin determination by ALCA (7A). After exactly 200 ml. water was added, shaking was continued for 4 hr., and it was found that further shaking did not increase the chloride content of the solution.

Filter the solution by means of a Buchner funnel with Whatman 42 paper, using a suitable filter aid and discarding the first portion of the filtrate.

If the filtrate is close to neutral, titrate an aliquot with 0.1*N* silver nitrate; acids and alkalies have to be neutralized first. If the filtrate contains sulfides, apply the method of Lohlein-Volhard, and proceed as recommended for beamhouse liquors by ALCA (7).

If V' ml. filtrate consumed V'' ml. silver nitrate of factor f,

$$\text{Percent NaCl} = \frac{2.338\ f\ V''\ (100 - M)}{100 - M'}$$

The following results were obtained when comparing this method with incineration:

Shaking method	11.8%	14.3%	12.9%
Incineration	11.9%	14.1%	12.1%

According to these tests, the full amount of chlorides could be found by the shaking method in all cases.

Procedure in the presence of excessive grease.—Special measures have to be taken if the specimens contain excessive grease which smears up the Wiley mill and prevents uniform grinding and mixing. This hardly ever occurs on hides after fleshing, more often on samples from the lime or from the soak, and most frequently on raw hides. Grease in lumps on the flesh side may be recognized easily, and in those rare cases when there are no lumps but the whole hide is penetrated by excessive grease this can be recognized by the soft feel of the specimen.

In such cases break up the predried and conditioned specimen into pieces which fit the regular fat extraction thimbles, and extract with petroleum ether in the Soxhlet. As a rule the extraction has to be extended to 16 hr., because these pieces are more difficult to extract than the ground specimen. After extraction spread the substance in the open air for 24 hr. in order to evaporate all petroleum ether and to restore the equilibrium with the humidity of the air.

This predried, fat-free material has to be weighed and ground by the regular way and used for all determinations with the exception of the fat content.

Calculation will be a little different because the fat content F has to be taken into consideration too. Moisture M is calculated as follows:

$$M = \frac{PM + M'(100 - PM - F)}{100}$$

In all other equations the expression $(100 - M)$ has to be replaced by $(100 - M - F)$. Thus,

$$FC = \frac{0.5608\ V\ f\ (100 - M - F)}{100 - M'} \text{ etc., etc.}$$

RESULTS

There were not enough figures available to establish extreme limits or characteristic averages for any stage. Only a few observations will be reported here.

Salt-cured raw hides have somewhat higher salt content and lower moisture content than brine-cured ones. The salt content amounted to 12–16% in salt cure and to 10–15% in brine cure. After the hides were soaked for 24 hr. in 400% water of 70°, about 1/3 of the original salt content could still be found, although soaking was preceded by a 10-min. wash with flowing water in the paddle. When the hides were limed in the same amount of float, at the same temperature, for 48 hr., the salt content decreased to about 1/20 of the original. The moisture content amounted to 35–45% in salt cure and to 40–55% in brine cure, and increased during soaking gradually, at a fairly slow rate, ending at 70% after 24 hr.

The pH of limed hides was only slightly lower than the pH of the lime liquors, averaging about 11. In subsequent operations a certain divergency could be observed, the pH of the hides being considerably higher than the pH of the surrounding deliming, bating, and pickling liquors; this proves that no perfect equilibrium may be reached under the practical conditions of a tannery.

Total alkalinity was lower than 0.6%, and free causticity was lower than 0.3%, in all cases. Deliming and bating operations which were based upon ammonium salts and commercial bates had very little influence upon total alkalinity, but they decreased free causticity, sometimes even as far as zero. The hides became more flaccid and better bated with decreasing free causticity. Total alkalinity could be influenced substantially by acids, and thorough pickling reduced it to zero.

Shoulders had higher moisture and lower hide substance contents than butts.

CONCLUSION

Methods were demonstrated which could be applied successfully to the testing of raw hides and of hides in process. Different raw hide cures and different stages of the process yielded characteristic alterations in the figures, and specifications of characteristic values may be valuable means of raw material and plant control.

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REFERENCES

1. *Methods of Sampling and Analysis*, ALCA B3.
2. *Ibid.*, B20.
3. *Ibid.*, B2.
4. *Ibid.*, B4.
5. *Ibid.*, B5.
6. *Ibid.*, B15.
7. *Ibid.*, F50.

7A. *Ibid.*, A22.

8. H. R. Procter. *Leather Industries Laboratory Book*, 357 (1908).
9. *Ibid.*, 101.
10. H. R. Procter. *Leather Chemists' Pocket Book*, 184 (1912).
11. *Ibid.*, 43.
12. Bergmann-Grassmann. *Handb. der Gerbereichemie u. Lederfabrikation*, Vol. 3, Part 1, 849 (1936).
13. A. Küntzel. *Gerbereichemisches Taschenbuch*, 267 (1955).
14. VAGDA. *Gerbereichemisches Taschenbuch*, 73 (1932).
15. Central Scientific Co. Catalogue J. C. 154, 346.
16. *The Laboratory*, **27**, 2, 50 (1958).
17. J. A. Wilson and H. B. Merrill. *Analysis of Leather*, 11 (1931).
18. A. Colin-Russ. *J. I.S.L.T.C.*, **15**, 113 (1931).
19. J. Mitchell and D. M. Smith. *Aquametry* (1948).
20. J. Marcusson. *Mitt. kgl. Materialprufungsamt*, 23, 58 (1905).
21. ———. *Z. angew. Chemie*, **18**, 754 (1905).
22. H. Scholz. *Das Leder*, **3**, 218 (1952).
23. J. Jany. *JALCA*, **50**, 5 (1955).

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We can hardly afford an aggravation of the widening intellectual gulf between science and other facets of human activity. We should confess a growing concern over the recurrence of hostile issues that are splitting the scientists themselves into various camps. The recent marked increase in the odd group of functional specialists who use political methods for advancing their scientific positions—the political physicists, the political chemists, the political professors, the political doctors, and other politically lacquered scientists—has poured fuel on this fire of dissension. We should remember that the loss of the will of functional groups to cooperate has been one of the main causes of the disintegration of great civilizations in the past. We should regain the spontaneity of intuitive cooperation. —R. G. H. Siu, *The Tao of Science*, a joint publication of The Technology Press of M.I.T. and Wiley, 1957. © Massachusetts Institute of Technology.

LIFE LINES

Brief Biographies of Our Contributors

Dr. Theone C. Cordon received his B.S. and M.S. degrees from Utah State University and his Ph.D. from Rutgers University. He was associated with the New Jersey Experiment Station and the University of Idaho before becoming affiliated with the Eastern Regional Research Laboratory of the U. S. Department of Agriculture where he has conducted research on hides, tanning materials, and leather since 1942.

Alfred L. Everett is a graduate of Lehigh University, Bethlehem, Pa., receiving his degree in 1940. After almost five years in the Army he joined the staff of the Eastern Regional Research Laboratory, U. S. Department of Agriculture, in 1946. Since 1947 he has been concerned with research on hides and skins at the same location, now known as the Hides and Leather Laboratory, Eastern Utilization Research and Development Division. For the past several years he has conducted histological studies as part of the program on developing a process for enzymatic unhairing of hides.

Howard W. Jones is a graduate of Bucknell University, Lewisburg, Pa., where he received a B.S. degree in chemistry. He joined the staff of the Eastern Regional Research Laboratory, U. S. Department of Agriculture, in 1951, where he was engaged in steroid chemistry research until 1957. Since that time he has been concerned with research on hides and skins in the Hides and Leather Laboratory at the same location.

George K. Kardos is the descendant of a family of Hungarian tanners and learned the trade in his early childhood. After completing his studies in chemistry at the University of Szeged, Hungary, he served the Canadian leather industry for thirteen years as technician and superintendent. He also put the first tannery in Lower California into operation. One year ago he founded Euderma Consultants, an international leather consulting service.

Dr. Joseph Naghski since 1955 has been Head of the Hides, Tanning Materials and Leather Section of the Eastern Utilization Research and Development Division of the U. S. Department of Agriculture. He received

the B.S. degree from Cornell University, the M.S. degree from the University of New Hampshire, and the Ph.D. degree from Pennsylvania State University. He joined the staff of the United States Department of Agriculture's Eastern Regional Research Laboratory in 1941 where he has carried out research in various fields which include the chemistry and microbiology of tobacco fermentation, the chromatography of tobacco alkaloids, the chemistry of flavonoids, the chemistry and microbiology of maple sugar products, and microbiological processes for recovery of natural rubber. He is coauthor of a recent book entitled *Rutin and Related Flavonoids*.

William E. Palm is a technologist in the Product Properties Evaluation Investigations group of the Animal Fat Properties Laboratory, Eastern Utilization Research and Development Division, United States Department of Agriculture. Since joining the staff in 1943, he has conducted research primarily in the evaluation of natural and synthetic polymeric compositions through the examination and characterization of their mechanical properties.

Dr. Wallace Windus received his Bachelor's degree from the University of Montana and his Doctor's degree from the University of Illinois. He was employed by the Rohm & Haas Company from 1931 to 1944, during which period he was coauthor of several important papers on the mechanism of unhairing. He was then associated with John R. Evans and Company and the Tanimex Corporation. Dr. Windus joined the staff of the Eastern Utilization Research and Development Division of the United States Department of Agriculture in 1956 and is now Head of the Processing Investigations of the Hides and Leather Laboratory. He has been a member of ALCA since 1932 and has served as Councillor (1951-53). Since March, 1959, he has been Editor-in-Chief of *JALCA*.

Dr. Lee P. Witnauer, a graduate of Canisius College and Temple University, joined the staff of the Eastern Utilization Research and Development Division, U. S. Department of Agriculture, in 1943. He is presently Acting Chief of the Animal Fat Properties Laboratory and Adjunct Professor of Chemistry at Drexel Institute of Technology.

ALCA NEWS

Proceedings, Reports, Notices, and News

of the

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EMPLOYMENT NOTICES

WANTED: Chemist for a large midwest upper leather tannery. Must be able to set up pilot-plant testing program. Opportunity excellent. Replies will be kept confidential. Write to Box R-152, c/o Secretary, American Leather Chemists Association, University of Cincinnati, Cincinnati 21, Ohio.

Progressive tannery has opening for assistant chemist. We are looking for an ambitious young man with good educational background and some laboratory experience. Applicant will be given opportunity to familiarize himself with material and production control as well as test tanning and development work. Give full details which will be kept strictly confidential. Excellent opportunity for the right man. Reply to Box WR-443, c/o American Leather Chemists Association, University of Cincinnati, Cincinnati 21, Ohio.

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Ben A. Grota
William G. Quinn

The above slate of candidates has been prepared by the Nominating Committee.

Herbert L. Ellison
Ernest H. Stein
Frank Zeissig, *Chairman*

Members are requested to note that additional candidates may be nominated by petitions signed by 15 or more active members. Such petitions shall reach the Secretary not later than April 1 and shall contain a statement of the willingness of the nominee to serve if elected. No member shall sign more than one petition for each office to be filled.

The ancients, who wished to preserve the clear and good character of the world, first set about to regulate their national life. In order to regulate their national life, they cultivated their family life. In order to cultivate their family life, they rectified their personal life. In order to rectify their personal life, they elevated their heart. In order to elevate their heart, they made their will sincere. In order to make their will sincere, they enlightened their mind. In order to enlighten their mind, they conducted research. Their research being conducted, their mind was enlightened. Their mind being enlightened, their will was made sincere. Their will being sincere, their heart was elevated. Their heart being elevated, their personal life was rectified. Their personal life being rectified, their family life was cultivated. Their family life being cultivated, their national life was regulated. Their national life being regulated, the good and clear character of the world was preserved and peace and tranquillity reigned thereafter.
—Confucius, as quoted by R. G. H. Siu in *The Tao of Science*.

ABSTRACTS

Determination of the Thermosulfuric Index. G. Bigoni. *Olii minerali, grassi e sap ni, colori e vernici*, **37,** 49 (1960).—The temperature reached in the reaction between olive oil and concd. H_2SO_4 is lower than the temperatures attained in the reactions between the acid and all other oils, so that this method should be able to identify olive oil. But the determination made with the procedure and the apparatus of Tortelli, who first proposed this identification method (cf. *Chemiker Zeitung*, **33,** 135, [1909]), is very uncertain, and the result depends on the sp. g. of the acid, the exact shape and dimension of the apparatus and of the thermometers, etc. It is suggested that the International Commissions standardize the procedure in order to obtain more accurate results.
G.A.B.

Electrophoresis and Paper Chromatography of Some Esters of Gallic Acid. A. Baruffini. *Farmaco*, **14,** 747 (1959).—Some esters of gallic acid are used as antioxidants, but the mixtures of these esters cannot be separated by electrophoresis methods, because only some of the components show a certain mobility in the electric field, and the migration values are dependent on pH and in some cases give only scarcely perceptible displacements. With paper chromatography it is possible to separate nonyl ($R_f = 0.81$), decyl ($R_f = 0.66$), lauryl ($R_f = 0.44$), cetyl ($R_f = 0.09$), and stearyl ($R_f = 0.01$) gallate, by using a mixture of dioxane-Et acetate-H_2O (3:1:6) on Whatman paper No. 1. The gallates with low mol. weight (i.e., ethyl, propyl, and butyl gallates, which with the above method give a unique spot [$R_f = 0.90$]) may be separated either with $CHCl_3$-CH_3OH-dild.HCl (4:1:2) or with $CHCl_3$-Et acetate-dild.HCl (4:1:1).
G.A.B.

Determination of Fixed Fatty Matters in Chamois Leathers. A. Castiglioni and R. Airoldi. *Rassegna chim.*, **11,** No. 6, 13 (1959).—The direct method ordinarily employed in the determination of fixed fatty matters in chamois leathers (i.e., decomposition of the hide substance with alkalies in alcoholic solution, acidification, and extraction of the fatty acids with ether and ethanol) gives results lower (even by 50–70%) than those obtained with the indirect method, i.e., with the calculation of the difference between 100 and the sum of the other determinations, as it is done for the fixed tannin in the analysis of vegetable-tanned leather. From several experiments it results that in cod, sardine, and seal oil, after some months of contact with air, there is a progressive decrease of the I no., and of the soluble matters in ether or ethanol, while the total weight and the acidity increase. Linseed oil behaves in a rather similar manner. The fatty matters extracted with solvents from oils kept in contact with air are decreased after 6 months by 21.4% for cod oil, 24.7% for sardine oil, 22.5% for seal oil, and 17.7% for linseed oil. The transformations induced in the oils by the action of time and oxidation may explain the differences observed.
differences observed.
G.A.B.

Contribution to the Knowledge of the Constitution of Sumac Tannin. II. E. Durio, A. Catino, and A. Oddone. *Cuoio, pelli, mat. concianti*, **36,** 137 (1960); cf. *Ibid.*, **35,** 183 (1959).—In the fractionation with solvents of

tannin ext. from leaves of sumac (*Rhus coriaria* from Sicily), an acid fraction was isolated which contained only a brown powder which decomposed without melting when heated and gave no tannin reactions except precipitation with gelatin solution when in very concentrated solutions. By fractionation with the Craig apparatus (with solvents Et_2O-H_2O) it was possible to purify this compound, which had m.p. 239°–40° (with decomposition), and gave reactions of gallic acid. Other fractions contain some phenolic compounds which will be examined later. **III. The Double Refraction of Sections of Tanned and Untanned Hide.** *Ibid.*, **36,** 296.—It was previously observed that certain tannins cause the inversion of the micellar double refraction of hides; this phenomenon was examined following the theory of Wiener and considering the hide as a material formed by parallel-orientated little bars. The examinations were made with a polarizing microscope with a light of 512 mμ, and the readings were taken with an ellyptic compensator of Senarmont. Samples of hides, both untanned (but buffered with a citrate-HCl buffer at pH 4.1) and tanned with the whole sumac extract, and with the phenolic fractions previously separated by the Craig fractionation apparatus (cf. *Ibid.*, **35,** 183, [1959]), were dehydrated with the alcohol-xylene method and dipped in melted paraffin, and the sections were then examined. The untanned hide has a weak positive birefringence, while samples tanned with the whole extract show a negative birefringence. Samples tanned with phenolic fractions separated with the Craig apparatus (which show a tanning power even greater than that of the whole extract) do not show inversion of the birefringence. It is supposed that inversion is due to some constituents of the extract which are not among those having true tanning properties. G.A.B.

Application of the Lossen Rearrangement of Dinitrophenyl-hydroxamates to Analysis of Carboxyl Groups in Model Compounds and Gelatin. P. Gallop, S. Seifter, M. Lukin, and E. Meilman. *J. Biol. Chem.*, **235,** 2619–27 (1960).—Commercial pigskin gelatin was esterified (methanol, acetic anhydride) and hydroxamated by reaction at 40°C. with neutral aqueous hydroxylamine. The gelatin derivative was dinitrophenylated at pH 7. The DNP gelatin derivative was dissolved in warm water, and the Lossen rearrangement was carried out in 0.05*N* NaOH with heating for 2 min. at 100°C. Quantitative amino acid analysis (column chromatography) was obtained of the esterified gelatin, the gelatin-dinitrophenylhydroxamate, and the latter derivative after Lossen rearrangement. With the exception of aspartic and glutamic acids, amino acid concentrations were unaffected by the treatments. Compared with methylated gelatin, the Lossen-rearranged gelatin showed a decrease of 13 aspartic acid residues with a concomitant increase of 8.8 residues of diaminopropionic acid; however, a decrease of 39.6 glutamic acid residues was accompanied by appearance of only 8.4 residues of diaminobutyric acid. Succinic semialdehyde was demonstrated in the hydrolysate of the Lossen-rearranged gelatin-dinitrophenylhydroxamate indicating the probable existence of γ-glutamyl linkages in the treated gelatin. J.M.C.

Masked Condition of Ionic Residues in Collagen. H. Kern. *Biochim. Biophys. Acta.*, **42,** 348–51 (1960).—The distribution of NaCl between steer-hide collagen and external salt solutions was examined. Small collagen segments were equilibrated with various concentrations of NaCl for several days at 3°C. The collagen pieces were removed, blotted or pressed, weighed and dried in

vacuum, and reweighed. The dry protein was extracted several times with 2-ml. portions of 0.1*N* HNO_3, and Na and Cl were determined in the combined acid extracts and in the medium. Subjecting the collagen equilibrated with the NaCl medium to hydraulic pressures up to 10 tons increased the Cl^- concentration in the collagen phase relative to that in the medium but decreased the Na^+ conc. There appear to be negligibly few available free anionic sites compared to the number of available cationic sites in collagen. The excess of Cl^- associated with the collagen over and above that predicted by the Donnan relationship was observed to decrease with increasing concentrations of NaCl in the medium. It is speculated that only the excess (over the acidic) basic residues in collagen are available for interaction with NaCl and that 95% of the ionic sites in steerhide collagen most probably exist in some sort of internal compensation. J.M.C.

Infrared Examination of the Association of Cornea Proteins with Water. S. Bakerman and C. Mitchell. *Nature*, **187**, 1033–34 (1960).—Ox cornea has a water content of 75–80%; collagen makes up about 70% of the solids. The infrared spectra of the following preparations were examined: fresh cornea, cornea after drying 5 hr., cornea after drying 2 days, cornea dried 2 days and then immersed in water 30 min., and cornea dried 2 days and then immersed in water 2 days. The withdrawal of water from the tissue leads to structural changes of the cornea which are revealed by the infrared absorption bands found in the dried tissue. The inability to re-establish the infrared curve by adding water to the dried tissue indicates that the polar groups which were associated with water in the fresh cornea are no longer available. The loss of water in the cornea apparently breaks the association between the protein and water molecules. Since the final dried cornea is hard and has the physical characteristics of a high-molecular-weight polymer, it is suggested that the active polar groups of the released protein may then become reoriented among themselves to form higher-molecular-weight components. C.L.D.

Serotonin, A Melanocyte-stimulating Component in the Dorsal Skin Secretion of *Xenopus laevis*. F. C. Van de Veerdonk. *Nature*, **187**, 948–49 (1960).—The substance isolated from the dorsal skin secretion of the frog that is able to produce a concentration of the pigment granules in the melanocytes of isolated pieces of frog skin has been identified as serotonin. C.L.D.

Torsional Properties of Single Wool Fibers. I. Torque-Twist Relationships and Torsional Relaxation in Wet and Dry Fibers. T. W. Mitchell and M. Feughelman. *Textile Research J.*, **30**, 662–67 (1960).—An apparatus is described for the direct measurement of torque-twist relationships for single wool fibers. All the results obtained are consistent with a molecular model in which the matrix consists of a cross-linked polymer held together by a network of hydrogen bonds. C.L.D.

Kinetic Study of the Wool-Water System. II. Mechanisms of Two-Stage Absorption. I. C. Watt. *Textile Research J.*, **30**, 644–51 (1960).—The kinetics of the uptake of water vapor by wool is dependent on the initial concentration of water and the size of the concentration increment. For small concentration increments absorption may occur in two stages, the second stage

much slower than the first. First-stage absorption obeys Fick's laws of diffusion. Second-stage absorption is accompanied by irreversible configurational changes within the fibers. The hypothesis that in polymer-penetrant systems second-stage absorption occurs as a result of stress relaxation within the sorbent was tested for the wool-water system. C.L.D.

Phosphate Esters Produced by Mammalian Skin From 2-Deoxy-D-glucose. S. A. Brooks, J. C. Lawrence, and C. R. Ricketts. *Nature*, **187**, 1028–29 (1960).—Skin slices maintained in Krebs-Ringer phosphate medium containing 2-deoxy-D-glucose convert the latter into 2-deoxy-D-glucose-6-phosphate and D-mannonate-6-phosphate. C.L.D.

Gelatin and Glue Research. *Nature*, **187**, 998 (1960).—A review is given of the papers presented at the nineteenth meeting of the British Gelatine and Glue Research Association (May 19, 1960): I. "A Preliminary Study of the Thermal Conversion of Acid-Soluble Calfskin Collagen into Gelatin" by G. R. Tristram. II. "The Swelling of Gelatin Films" by E. M. Simms and J. N. Blake. III. "The Flocculation of Suspensions with Gelatin" by A. M. Kragh. C.L.D.

Abnormal Crimping in Merino and Polwarth Wools. R. E. Chapman, B. F. Short, and P. G. Hyland. *Nature*, **187**, 960–61 (1960).—An abnormal wool known as "doggy" wool is found in some older sheep of Merino and Polwarth flocks; it is characterized by reduced frequency of crimps, so that in extreme cases the fibers are almost straight. Preliminary evidence is presented that doggy wool is associated with hyperplasia and cyst formation of the outer root-sheaths of a considerable proportion of the follicle population of affected sheep. C.L.D.

Staining of Skin with Dihydroxyacetone. E. Wittgenstein and H. Berry. *Science*, **132**, 894–95 (1960).—The reaction of skin with dihydroxyacetone to produce a brown "artificial tan" appears to proceed through combination with free amino groups in skin proteins and particularly by combination of dihydroxyacetone with the free guanido group of arginine. C.L.D.

Studies on Post-Mortem Changes. II. Effect of Post-Mortem Period on the Hydrothermal Stability of Hide and Leather. S. C. Nandy and S. N. Sen. *Bull. Central Leather Research Inst. Madras*, **6**, 515–22 (1960); cf. abstr. *JALCA*, **55**, 707 (1960).—Freshly slaughtered, fleshed, washed cowhide was allowed to stale for 2 to 72 hr. at 30°C. in a moist atmosphere. The shrink temperature (T_s) was not affected by staling for 48 hr., but dropped about 1°C. after 72 hr. When the staled pieces were cured by wet-salting, dry-salting, or drying, and subsequently soaked, a slight decline in T_s was noted for pieces staled more than 24 hr., particularly for dried specimens. Dried specimens soaked 3 days had T_s about 1°–2°C. higher than non-dried specimens, for staling periods of 2 to 24 hr., and 2.5°–3.5°C. lower for staling periods of 48 and 72 hr. This indicates that the effect of drying is not completely reversed by soaking 3 days in plain water and that the damage caused by staling is somewhat enhanced by drying. Specimens that were soaked, limed, bated, Cr-tanned, and fatliquored and dried after staling showed a slight drop in T_s

at each stage for staling periods exceeding 24 hr. The effect was most noticeable after liming (in white lime at 20°C.) and increased with duration of liming up to 10 days. H.B.M.

Effect of Salts and Sulfonyl Chloride in Formaldehyde Tannage. Y. Nayudamma, K. S. Jayaraman, and D. Ramaswamy. *Bull. Central Leather Research Inst., Madras*, **6**, 577–87 (1960).—A continuation of work reported in *JALCA*, **52**, 238 (1957).—Acetone-dehydrated pelt was wet back and tanned for 3 days, at various pH values, with 50 ml. of 1% HCHO solution per 10 g. pelt, and 100 meq. salt per 100 g. hide substance. The tanned pelt was washed and analyzed for combined HCHO and collagen. Fixation of HCHO was increased by about 50% in the presence of NH_4Cl, $(NH_4)_2SO_4$, or $NH_4(CH_3COO)$ at pH values from 4.7 to 6.0, and by about 20% in the presence of either Fe(II) or Fe(III) sulfate at pH 3.5. Fixation was unchanged, or reduced slightly, in the presence of Na monochloroacetate, benzoate, succinate, fumarate, and malonate, all at pH 7.0; it was increased by about 20% in the presence of Na acetate, salicylate, and phenolsulfonate and by about 63% in the presence of Na aminoacetate and maleate. The influence of *cis-trans* isomerism in the cases of maleic and fumaric acids is noteworthy, as well as the opposite effects of substituting NH_2 and Cl in the acetate radical. In further experiments 10-g. portions of hide powder were soaked, drained, treated with 25% Immergan (a commercial hydrocarbon sulfonyl chloride, RSO_2Cl) for 3 or 4 days at pH values from 4 to 10, dried, freed from excess Immergan by extraction with acetone, retanned with HCHO, washed, dried, and analyzed for collagen, S, and HCHO. Comparison lots were tanned with HCHO at the same pH values without RSO_2Cl pretannage. Fixation of both S and HCHO increased with pH value, with a plateau near pH 5–7. Hide powder pretanned with RSO_2Cl fixed about twice as much HCHO at pH 4, 75% more at pH 7, and 50% more at pH 9, compared with untreated hide powder. These increases may be caused by activation of the guanidine groups at high pH values, and of acid amide groups at acid and neutral pH values. Isoelectric points were determined as follows: untanned collagen, 5; HCHO-tanned, 4.5; RSO_2Cl-tanned, 2.6; RSO_2Cl-tanned and HCHO-retanned, 2.6; and fish-oil-tanned, 2.8. It seems that RSO_2Cl reacts with all the basic groups, forming sulfonamides that are quite acid in nature. H.B.M.

A Process of Unhairing Skins and Hides by Enzymes from Germinated "Ragi" *(Eleusine Coracana)* for the Manufacture of Leather. S. M. Bose, W. Madhavakrishna and B. M. Das. *Bull. Central Leather Research Inst. Madras*, **6**, 590–92 (1960); see Indian patent 52013.—Ragi (a cheap millet) is washed thoroughly, steeped 24 hr., allowed to germinate for 72 hr., ground to a paste, diluted, and filtered. The filtrate from 1 lb. dry ragi is used to unhair 4–5 lb. soaked skin along with 5% salt and acetic acid to give pH 4.5. Time for hair loosening depends on temperature (3–4 days at 26°–32°C.), and the skins should be unhaired and scudded as soon as the hair is loose. Bating is unnecessary. After scudding, the skins are washed, pickled, and processed further as previously described (abstr. *JALCA*, **54**, 372 [1959]). H.B.M.

Isolation of a Glucoside from Myrobalans. J. B. Rao and K. N. S. Sastry. *Bull. Central Leather Research Inst. Madras*, **6**, 593 (1960).—An

aqueous solution of an ethyl acetate extract of myrobalans, that contained 97.76% tannin, deposited white crystals that were identified as a glucoside. H.B.M.

Can the Increase of Carbon Dioxide Concentration in the Atmosphere Make Natural Waters More Corrosive and Harder? G. Bianucci and L. Ghiringhelli, *Acq. industr.*, **2**, No. 7–8, 53 (1960).—Until some years ago (about to 1900) the CO_2 concentration in the atmosphere averaged 300 p.p.m. by volume (although it might change considerably according to meteorological conditions); recent determinations show that it is now approximately 320 p.p.m.; and it is possible to calculate by extrapolation that it will reach the value of 360 p.p.m. in the year 1990 (if the behavior of the phenomenon does not undergo changes). The causes of this increase are principally the combustion of great quantities of fossil fuels (coal, methane, petroleum, etc.) and the decrease of forested areas, which causes a decrease of the CO_2 absorbed by the plants. CO_2 is then dissolved by rain water, and if the water flows on calcareous or magnesic soils, it dissolves great amounts of salts and becomes harder, while at the same time the greater amount of CO_2 dissolved makes the water more corrosive. G.A.B.

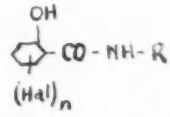
Ultrasonic Degradation of Wool and Hair. J. Bradbury, *Nature*, **188**, 207–08 (1960).—Preliminary experiments on ultrasonic degradation of wool and hair samples are discussed. The method offers advantages in a study of the chemical composition and structure of the various cuticle layers of wool. C.L.D.

Differential Thermal Analysis of Protein Fibers. R. Schwenker and J. Dusenbury, *Textile Research J.*, **30**, 800–01 (1960).—From the results of differential thermal analysis of keratin fibers, conclusions are drawn on the structure of the protein. C.L.D.

PATENTS

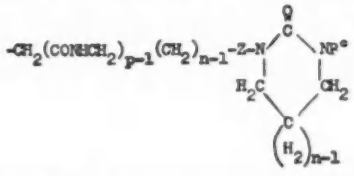
Filling Leather Brit. Pat. 832,664. Farbenfabriken Bayer A.G. Appl. May 7, 1958.—Leather is filled by treating it with an aqueous dispersion of finely-divided fillers in the presence of water-soluble dispersing-agents precipitable by acids, said agents being obtained by condensation of one or more carbamides (such as dicyandiamide) with formaldehyde in a non-acidic medium containing a water-soluble salt of an organic sulphonic acid (such as the sodium salt of dinaphthyl methane disulphonic acid) and finishing the treating process by adjusting to an acid *p*H value. The addition of acid reagent for adjustment may be dispensed with if the leather possesses at the end of the treatment a high acidity. The products to be used as dispersing agents may be obtained as in Specification 827,473, or in U.S.A. Specifications 2,737,504 and 2,884,403. The fillers used include finely-divided silicic acid, aluminium oxide, carbon black, iron oxide pigments, china clay, talc, and other specified inorganic fillers, or organic fillers such as polyvinyl chloride, cellulose, starch and its ethers, and other specified organic fillers.

Proofing Permeable Materials. Brit. Pat. 834,576. Geigy A.G., J. R. Appl. July 20, 1956.—Protection of cellulose textiles, paper, leather, or vegetable or animal mucilage from fungal attack, rot or mildew spots is obtained by impregnating them with, or incorporating in them, salicyclic acid-*n*-amylamide or a compound of formula



wherein R represents the saturated hydrocarbon radical containing 3 to 6 carbon atoms, HAL represents halogen and *n* represents an integer of 0 to 3. Specified compounds are 5-chloro- or bromo-salicyclic acid-*n*-amylamide, 3,5-dichloro-salicylic acid-*n*-amylamide, 5-chloro-salicylic acid cyclohexylamide, 5-chloro-salicyclic acid-*n*-propylamide, 5-chloro-salicyclic acid isoamylamide and 5-chloro-salicyclic acid-*n*-hexylamide. The compounds may be used in aqueous or organic solution.

Coated Fabrics; Waterproofing; Strengthening and Preserving Paper. Brit. Pat. 834,410. Rohm & Haas Co. Appl. March 13, 1956.—Water-repellent or waterproof properties are conferred upon substrates of leather and textile materials made from wool, cellulose, cellulose acetate, cellulose acetate-butyrate, polyvinyl alcohol, nylons, acrylamide and methacrylamide polymers, polyethylene terephthalate, polyacrylonitrile and vinyl chloride-acrylonitrile copolymers by coating or impregnating them, e.g. from aqueous or alcoholic solution, with a polymer or copolymer of an unsaturated ester, amide or ether containing quaternary ammonium groups attached to the polymer chain (*see* Group IV (a)) and having attached to the quaternary ammonium nitrogen atom a radical of the formula—$CH_2(CONH)_mR''$ or of the formula



wherein *m* is an integer of 1 or 2; R'' is H, —CH_2OH or CH_2OR^5, where R^5 is a C_1—C_5 alkyl group; *p* is an integer of 1 or 2; *n* is an integer of 1 or 2 when *p* is 2 but only 1 when *p* is 1; and Z is

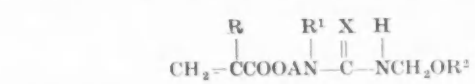
or —CH_2— when *p* is 1 but only —CH_2— when *p* is 2. After application to the substrate polymers in which R'' is hydrogen may be insolubilized by treatment with an aldehyde followed by heat treatment; those polymers in which R'' is a methylol or alkoxymethyl group may be insolubilized by heat treatment alone. Is is suggested that during heat treatment the polymer may react with the substrate. For application to textiles the polymers may be combined with auxiliary agents such as heat-convertible urea- and melamine-formaldehyde con-

densates. The above polymers may also be incorporated in paper, for example they may be added to paper pulp in a beater, for imparting high wet-strength to the paper. Polymers in which R'' is hydrogen also function as bactericides, fungicides and insecticides. Specifications 777,488 and 834,411 are referred to.

Paper; Leather Substitute; Agglutinated Fibre Fabrics; Coated Fabrics; Laminates. Brit. Pat. 833,679. Du Pont de Nemours & Co., E.I. Appl. July 18, 1956.—A fibrous structure which may be bonded by means of heat and pressure is made by forming a batt of fibres and impregnating it uniformly with an aqueous dispersion comprising the polymeric reaction product of a mixture of monomers comprising (A) acrylonitrile, (B) an α-olefinic carboxylic acid, and (C) an ester of one or more α-olefinic carboxylic acids with a saturated aliphatic C_1 to C_{12} monohydric alcohol, wherein the weight ratio of A to C is within the range 20:80 to 85:15, and B is 1.5 to 15% by weight of the total monomer mixture. Suitable fibres are polyethylene terephthalate (hereinafter referred to as polyester fibres), nylon, wood pulp, glass, polyacrylonitrile, viscose rayon, polyvinylidene chloride, polytetrafluoroethylene, polyurethane, cotton, jute and mixtures such as nylon and rayon, ground wood pulp and chemical wood pulp, and wood pulp and nylon. By appropriate choice of the ratio A:B:C and the ratio binder: fibre, paper-like, leather-like, or rigid final bonded products may be produced. Paper-like sheets may be produced by applying heat and pressure to the products prepared by impregnating a water-leaf of (a) nylon, polyethylene terephthalate, or a nylon-bleached kraft pulp mixture, the synthetic fibres having been dip-coated in a mixture of the surface-active agents sodium lauryl sulphate and lauryl pyridinium chloride, or (b) wood pulp or acrylonitrile with an aqueous dispersion of a copolymer M of a monomer mixture comprising acrylonitrile (A), butyl acrylate (B), and methacrylic acid (C) in the ratio 35:60:5 together with sodium bisulphite and potassium persulphate as polymerization initiators and sodium lauryl sulphate as dispersing agent. The impregnated acrylonitrile fibre material before curing may be twice dip-coated in a mixture of the copolymer M and a small proportion of a water-soluble heat-reactive phenol-formaldehyde resin together with a small amount of ammonium hydroxide solution, followed by curing with heat and pressure to produce electrical insulation unaffected by hydrocarbon lubricant oils and haloalkane refrigerants. A semi-rigid porous leather-like material suitable as a seal for oil, grease, and organic liquids may be produced from a pre-shrunk needled bath of polyester fibres impregnated with the copolymer M. A leather-like material suitable for belts and shoe uppers and insoles may be produced from pre-shrunk needled batt of eight crosslapped plies of polyester fibres impregnated with a copolymer containing 2-ethylhexyl acrylate instead of butyl acrylate as in the copolymer M, the impregnated batt being dipped in an aqueous solution of an inorganic salt, such as calcium, barium, zinc, cadmium or ferric chloride, aluminium sulphate, or strontium, lead, nickel or cobalt nitrate, to effect coagulation on the fibres. A pipe resistant to organic solvents is produced by curing in a mould an uncured web of polyester fibres wrapped spirally about a mandrel, the web having been impregnated with a copolymer N comprising 9 parts by weight of a mixture of the monomers (A), (B), (C) above but in the ratio 63:32:5 together with a dispersing agent and polymerization initiators as above and 1 part by weight of a 33% aqueous dispersion of a heat-reactive phenol-formaldehyde resin. Electrical insulation for use as slot liners for motors and generators may be prepared by heating under pressure a similar thin uncured web between sheets of polyethylene

terephthalate, or by curing a non-woven web of glass fibres impregnated with the copolymer M. Such a glass fibre sheet may also be post-formed into structural panels, pipes, or ducts. A blank for printed circuit production may be produced by bonding a copper foil with a synthetic resin adhesive to a batt formed by four plies of polyester fibres impregnated with the copolymer N, while a rigid structural panelling may be formed from a needled batt of similar fibres similarly impregnated and cured between glass fabric sheets having coatings of polytetrafluoroethylene on their inner faces. Specifications 761,928 and 787,900 are referred to.

Leather; Paper Containing Synthetic Polymers; Proofing Paper, Fabrics, Leather &c. Brit. Pat. 831,635. Rohm & Haas Co. Appl. April 12, 1956.—Homopolymers and copolymers of compounds of general formula

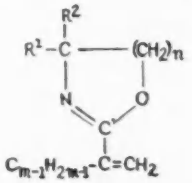


in which R is H or CH_3; A is a phenylene group or an alkylene group having 2–4 carbon atoms of which a chain of at least 2 extends between the adjoining O and N atoms; R^1 is a C_4–C_{12} alkyl group containing a tertiary carbon atom attached to the adjoining N atom, X is O or S, and R^2 is an alkyl group, may be dissolved in a suitable solvent containing an acid catalyst and applied to paper, leather, textiles, wood, metal, glass and plastics as coatings, adhesives or impregnants, as a preservative or pesticide, or to impart water-repellency. The materials are then dried to convert the polymers to insoluble and infusible condition. In the case of paper the polymer may be incorporated in the pulp, at the beater, or as it proceeds to the wire of the paper machine. Water-repellency may be imparted to leather when the polymers contain long-chain R^1 groups or hydrophobic groups are present in the comonomers. In the examples: (a) N - methoxymethyl - N - *t* - butyl - N^1 - methacrylatoethylurea, $CH_2 = C(CH_3)COOCH_2CH_2—N(C_4H_9\text{-}t)CONHCH_2OCH_3$ is dissolved in a low alcohol containing butyl acid phthalate (or butyl phosphoric acid) applied to a material such as leather, glass or wood, and the material is dried at 220°F.; if desired, the surface may be treated with an amine such as lauryl amine or with resins such as maleic polyesters in styrene solution; (b) N - *t* - butyl - N - methacrylatoethyl - N^1 - methoxymethylthiourea, $CH_2 = C(CH_3)COOCH_2CH_2\text{-}N(t\text{-}C_4H_9)CSNHCH_2OCH_3$ in solution containing an acid catalyst such as butyl phosphoric acid or ammonium chloride, and applied to materials such as textiles, wood, cellulosic materials and leather and the treated material dried and cured; the treated material may be further treated with an amine such as laurylamine; (c) a polymer prepared from $CH_2 = C(CH_3)COOCH_2CH_2\text{-}N(C_4H_9\text{-}t)CONHCH_2OCH_3$ by heating in butanol solution in the presence of benzoyl peroxide is used for the preparation of coatings for leather, metal, fabrics and the like; preferably butyl phosphoric acid is present and the material is cured by baking; and (d) a polymer prepared from $CH_2 = C(CH_3)COOCH_2CH_2N(t\text{-}C_4H_9)CSNHCH_2OCH_3$ by heating in butanol solution in the presence of benzoyl peroxide is used as coating for metals or plastics; it may also be applied to leather or textiles as a preservative and pesticide.

Waterproofing Leather. Brit. Pat. 834,033. General Electric Co. Appl. Sept. 24, 1957.—Leather, particularly suede leather, is water-proofed by apply-

ing thereto, as by dipping, swabbing, brushing or spraying, a composition comprising by weight (1) 9 to 19% of the intercondensation product of (a) a cohydrolysate of a trialkylsilane and an alkylsilicate, the alkyl radicals being lower alkyl radicals and the cohydrolysate containing Si-bonded OH groups, and (b) a high viscosity linear organopolysiloxane liquid containing terminal Si-bonded OH groups, (2) 9 to 19% of a hydrolysed lower alkyl silane containing a curing agent, (3) 24 to 34% of $Ti(OR)_4$, wherein each R is an alkyl radical having less than 13 C atoms, and (4) 38 to 48% of a solvent (*see* Group IV (a)).

Proofing Permeable Materials; Leather and Paper. Brit. Pat. 834,308. Rohm & Haas Co. Appl. May 7, 1957.—New compounds, e.g. oxazines and oxazolines, of the formula

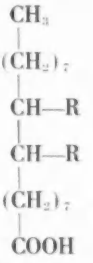


in which R^1 and R^2 when taken individually are alkyl radicals, one being methyl and the other having from 1 to 8 carbon atoms, or taken together form a divalent saturated aliphatic hydrocarbon group containing 4–9 carbon atoms which together with the carbon atom to which R^1 and R^2 are both bonded form a 5- or 6-membered ring, *n* is 1 or 2 and *m* is 1 or 2, are used for the treatment of cellulosic material such as paper and cloth fabrics for protection from mould or fungi attack. For such purpose the monomers may be added to paper and textile compositions such as paper sizing compositions, textile compositions, dressings and conditioning compositions for rendering fibres, yarns and filaments more amenable to processing, conditioning, spinning, weaving or knitting. They may also be used for waterproofing (Example 12) or be added as inhibitors for fungi or moulds in compositions used in leather treatment or other coated articles. Polymers and copolymers obtained from the new monomers may also be used for treating leather and for providing creaseproof coatings for paper.

Hide Tanning Process with Salt of Polymeric Acid Resinous Condensate of Organic-Oxo and Organic Nitrogen Compounds. U. S. Pat. 2,956,854. J. Plapper and R. Heyden, Dusseldorf, Germany, assignors to Bohme Fettchemie G.m.b.H., Dusseldorf, Germany. Filed Aug. 2, 1955.—1. The method of tanning animal hides which comprises contacting said hides sequentially with aqueous solutions of water-soluble salts of a polymeric acid selected from the group consisting of polymeric silicic acid and polymeric phosphoric acid and with aqueous solutions of water-soluble cation-active resinous compounds formed by condensing an organic oxo- compound selected from the group consisting of formaldehyde, acetaldehyde, acrolein, furfural and methylethylketone with an organic nitrogen compound selected from the group consisting of urea, thiourea, methylenediurea, cyanamide, guanidine, alkylguanidines, dicyandiamide, dicyandiamidine, guanamine, ammeline, ammelide and melamine, at a pH of between about 3.5 to about 4.5.

Process of Finishing Leather. U. S. Pat. 2,957,783. K. Dachs, R. Schubert, and H. Wilhelm, all of Ludwigshafen (Rhine), Germany, assignors to Badische Anilin- & Soda-Fabrik Aktiengesellschaft, Ludwigshafen (Rhine), Germany. Filed May 14, 1957.—5. Process which comprises finishing leather with a softener-free solution in a 1 to 4 carbon atom alcohol, of a polyamide of which 100 parts by weight of the polyamide-forming stock contain the following components:

(A) 15 to 85 parts by weight of a dicarboxylic acid of the formula



wherein one R stands for H and the other R stands for COOH, plus the equimolecular amount of a diamine of the formula $H_2N—X—NH_2$;

(B) 85 to 15 parts by weight of at least one polyamide-forming material selected from the group consisting of

(*a*) caprolactam,
(*b*) capryllactam,
(*c*) oenanthlactam, and
(*d*) a dicarboxylic acid with from 6 to 10 carbon atoms in the molecule plus the equimolecular amount of a diamine of the formula $H_2N—X—NH_2$ wherein X is a diradical with from 2 to 10 carbon atoms.

Rapid Process for Tanning Hides. U. S. Pat. 2,955,904. D. Schnoller, Pueyrredon Ave., 1256, Buenos Aires, Argentina. Filed Sept. 11, 1956.—1. A process for tanning hides comprising the steps of partially tanning the hides with a non-vegetable tanning agent for several hours to separate the fibers, mechanically expressing water from the partially tanned hides to reduce the weight of the partially tanned hides to an amount at least 30% less than the original weight of the hides, and tanning the hides with a vegetable tanning extract selected from the group consisting of dry, powdered tanning extracts and concentrated solutions thereof for several hours until the tanning extract has been absorbed by the hides in an amount about equal to the weight of the water removed during the expressing step.

Coated Fabrics. Brit. Pat. 831,898. Rohm & Haas Co. Appl. July 17, 1957. —Surfaces of textile fabrics, leather, paper, metals, glass, wood, vitreous and plastic materials, and cardboard are coated with compositions comprising (a) 5 to 95 parts by weight of a linear, water-insoluble, thermoplastic copolymer of (1) 1 to 10 mol. per cent of acrylic, methacrylic or itaconic acid; and (2) 90 to 99 mol. per cent of at least one alkyl ester of acrylic or methacrylic

acid; and (b) 95 to 5 parts by weight of a thermosetting resin-forming alkoxymethyl aminoplast condensate in which the alkoxymethyl group has from 2 to 19 carbon atoms, the amount of aminoplast being sufficient to provide 1.5 equivalents of oxymethyl groups per equivalent of carboxyl groups in the copolymer and the sum of the parts of copolymer and aminoplast being 100. The compositions may also contain specified pigments and solvents (*see* Group IV(a)) and may be applied by spraying, dipping, brushing or oil transfer, then dried and cured by heating to a temperature of from 200° to 400°F.

Production of a Tanning Agent from Waste Sulphite Liquor by Solvent Extraction. U. S. Pat. 2,952,507. H. B. Marshall, Toronto, Ontario, and A. C. Shaw, Don Mills, Toronto, Ontario, Canada, assignors to Ontario Research Foundation, Toronto, Ontario, Canada. Filed Nov. 24, 1958.—1. A process for making a tanning agent which comprises the steps of concentrating waste sulphite liquor to a solids content of between 25% and 65%, extracting effective tannins from the concentrated waste liquor with a water miscible alcohol that is capable of forming two phases with concentrated sulphite waste liquor, said alcohol being in an amount that will extract between 15% and 65% of the sulphite liquor solids, separating the alcohol rich phase, and stripping the alcohol from the alcohol rich phase to leave a tanning agent.

Method of Controlling the Finishing of Leather. U. S. Pat. 2,952,563. V. G. O'Gorman and J. G. Hollick, Beverly, Mass., assignors to United Shoe Machinery Corporation, Flemington, N. J. Filed Mar. 1, 1954.

The steps in the method of leather finishing which include the application to the surface of a leather work piece of one coating of a solution of a seasoning compound containing one critical component and a radioactive ingredient which emits one form of radioactive ray, the level of activity of which is in a known ratio to a unit of volume of the compound, applying a second coating of a solution of a seasoning compound containing a second critical component and a radioactive ingredient which emits a second form of radioactive ray, the level of activity of which is in a known ratio to a unit of volume of the second compound, measuring independently the amount of radiation of each of said radioactive ingredients per unit of area emanating from the coatings following their application to determine the amount of seasoning compound applied to the work piece by each of said coatings, and controlling the rate of application of each of said coatings to maintain the amount of seasoning compounds applied within predetermined limits.

Process of Tanning Hides with a Condensation Product of an Acid Salt of a Phenyl Amine, an Acid Salt of a Lower Alkyl Amine and Paraformaldehyde. U. S. Pat. 2,955,012. A. Küntzel and K. Rosenbusch, Darmstadt, Germany, assignors to Farbenfabriken Bayer Aktiengesellshaft, Leverkusen, Germany. Filed July 28, 1954.—1. A process of tanning hides which comprises pretanning the hides with an acid solution of a cationic tanning agent, said tanning agent being the condensation product obtained by melting at a temperature of about 140°C. stoichiometric amounts of an acid salt of a phenyl amine from the group consisting of aniline and lower alkyl substituted aniline, an acid salt of an amine from the group consisting of lower alkyl amine, hydroxy lower alkyl amine and dicyanodiamidine, and paraformaldehyde, and precipitating the condensation product from the melt, the amino group of the phenyl amine remaining free in the condensation product; and effecting finish tanning by gradually neutralizing said tanning solution.

Process for Tanning Leather with Water-Insoluble Condensation Product of a Phenol, Formaldehyde, and Carboxylic Acid. U. S. Pat. 2,955,013. M. Meister, Leverkusen-Wiesdorf, W. Luck, Koln-Stammheim, and G. Mauthe, Opladen, Germany, assignors to Farbenfabriken Bayer Aktiengesellschaft, Leverkusen, Germany. Filed Sept. 3, 1958.—1. A process for the preparation of leather which comprises subjecting a member selected from the group consisting of a material tanned and to be tanned with mineral tanning agents to the action of aqueous solutions of alkaline salts of condensation products which contain both phenolic hydroxyl and carboxyl groups and in the form of their free acid are water-insoluble, and acidifying the leather in the liquor to a pH value between 2 and 6 at which the condensation products are completely precipitated in the liquor.

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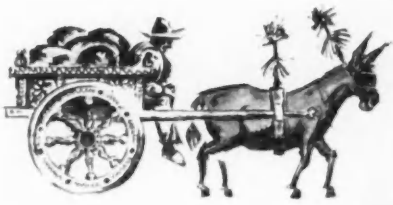

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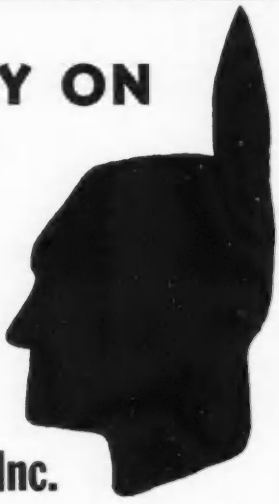

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Exclusively a Tannery Paper

Devoted to Leather Technology, Tanning and Finishing of Leather, Tannery News and Markets.

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